

CALCULATION OF THE RATE CONSTANTS OF A PHOTOCHEMICAL SYSTEM WITH THREE COMPONENTS

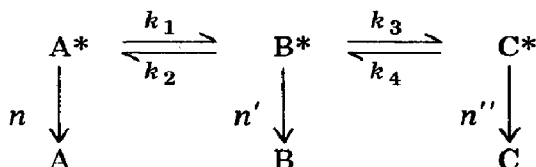
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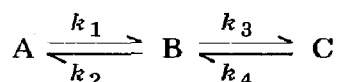
Summary

Analytical expressions for the rate constants k_i and $n^{(i)}$ of the photochemical reaction scheme:



with steady-state, modulated and pulsed excitation of A are derived.

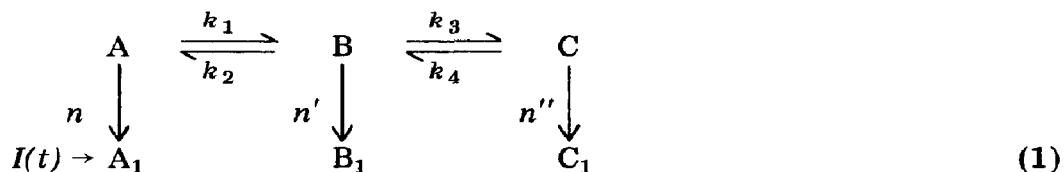
The evaluation of kinetic rate constants k_i of a three-component system:



in the ground state is described in the literature [1]. Steady-state and transient (relaxation) methods are used. The present state of experimental development has been described in a book [2]. Kühne and Walter [3] have reported on special mathematical procedures and methods for analysis of the equilibrium.

A photochemical system with three components is involved in the change in the fluorescence spectrum of aromatic carbon acids [4], and possibly also in the diabatic deactivation of naphthalene derivatives [5, 6].

The general photochemical system is:



A, B and C are the concentrations of the electronic excited states of the components A_1 , B_1 and C_1 ; k_i the photochemical and $n^{(i)}$ the photophysical rate constants; $I(t)$ the excitation intensity. It is assumed that the photons are absorbed only by A_1 . In the case of the protolytic fluorescence change of 1-naphthol (ROH) we have: $A = \text{ROH}^* + \text{H}_2\text{O}$, $B = (\text{ROH} \cdot \text{H}_2\text{O})^*$, $C = \text{RO}^{-*} + \text{H}_3\text{O}^+$ and $k_4 = k'_4 [\text{H}_3\text{O}^+]$. The reaction scheme (1) leads to the following system of differential equations:

$$\begin{aligned} \frac{dA}{dt} &= -(n + k_1)A + k_2 B + I(t) \\ \frac{dB}{dt} &= k_1 A - (n' + k_2 + k_3)B + k_4 C \\ \frac{dC}{dt} &= k_3 B - (n'' + k_4)C \end{aligned} \quad (2)$$

To determine the constants experimentally three methods can be used to disturb the equilibrium: steady-state [$I(t) = I_0 = \text{const.}$], modulated [$I(t) = e^{i\omega t}$] and step- or delta-shaped [$I(t) = 1$ for $t = 0$ and $I(t) = 0$ for $t > 0$].

Steady-state excitation

In the stationary case, the concentrations are time-independent: $dA/dt = dB/dt = dC/dt = 0$. The system (2) is reduced to:

$$\begin{aligned} -(n + k_1)A + k_2 B &= -I_0 \\ k_1 A - (n' + k_2 + k_3)B + k_4 C &= 0 \\ k_3 B - (n'' + k_4)C &= 0 \end{aligned}$$

By using Cramer's rule the solution may be shown to be:

$$A = \frac{D_A}{D}, \quad B = \frac{D_B}{D}, \quad C = \frac{D_C}{D}$$

D is the coefficient determinant: $D = -(nn' + n'k_1 + nk_2)(n'' + k_4) - (n + k_1)n''k_3$. The Cramer's determinants are:

$$\begin{aligned} D_A &= -I_0 [(n' + k_2)(n'' + k_4) + k_3 n''] \\ D_B &= -I_0 k_1 (n'' + k_4) \\ D_C &= -I_0 k_1 k_3 \end{aligned}$$

The intensity I_0 can be eliminated by using A_0 as a reference {e.g. for the fluorescence change of 1-naphthol: $A_0 = A([\text{H}_3\text{O}^+] \rightarrow \infty)$ }.

Harmonically modulated excitation: $I(t) = e^{i\omega t}$

ω means the frequency of modulation. The particular solution of system (2) for this type of excitation is:

$$A(t) = a e^{i(\omega t - \varphi_1)}$$

$$B(t) = b e^{i(\omega t - \varphi_2)}$$

$$C(t) = c e^{i(\omega t - \varphi_3)}$$

where a , b and c are the degrees of modulation of the emission and the φ_i the phase difference between the signals due to the emission and the excitation. By using the Cramer's rule we obtain:

$$a e^{-i\varphi_1} = \frac{D_A}{D}, \quad b e^{-i\varphi_2} = \frac{D_B}{D}, \quad c e^{-i\varphi_3} = \frac{D_C}{D}$$

and so:

$$\tan \varphi_1 = \frac{\text{Im}(D^* D_A)}{\text{Re}(D^* D_A)}$$

and similarly for φ_2 and φ_3 substituting B or C for A:

$$D = \begin{vmatrix} i\omega + n + k_1 & -k_2 & 0 \\ -k_1 & i\omega + n' + k_2 + k_3 & -k_4 \\ 0 & -k_3 & i\omega + n'' + k_4 \end{vmatrix}$$

D^* denotes the conjugate complex of D . D_A , D_B and D_C may be obtained by the method of the previous section. Substituting these determinants into the formula for the tangent, we obtain by simple algebra:

$$\frac{\tan \varphi_1}{\omega} = \frac{\omega^2 a_1 b_2 + a_3 b_1 - a_2 b_2}{\omega^2 (a_3 b_2 - a_1 b_1) + a_2 b_1}$$

$$\frac{\tan \varphi_2}{\omega} = \frac{\omega^2 a_1 - a_2 + a_3 (n'' + k_4)}{\omega^2 [a_3 - a_1 (n'' + k_4)] + a_2 (n'' + k_4)}$$

$$\frac{\tan \varphi_3}{\omega} = \frac{a_3}{a_2 - \omega^2 a_1}$$

where

$$a_1 = n + n' + n'' + k_1 + k_2 + k_3 + k_4$$

$$a_2 = (n'' + k_4) (nn' + n'k_1 + nk_2) + n''k_3(n + k_1)$$

$$a_3 = -\omega^2 + nn' + n'k_1 + nk_2 + nk_3 + k_1k_3 + n''k_3 + (n'' + k_4) \times \\ (n + n' + k_1 + k_2)$$

$$b_1 = -\omega^2 + n''k_3 + (n'' + k_4)(n' + k_2)$$

$$b_2 = n' + n'' + k_2 + k_3 + k_4$$

The solution for the degrees of the modulation is not given because their experimental determination is complicated and inexact especially at higher frequencies.

Pulse excitation: $I(t) = 1$ for $t = 0$ and $I(t) = 0$ for $t > 0$

By using $A = A_0 \exp(-\lambda t)$, $B = B_0 \exp(-\lambda t)$, $C = C_0 \exp(-\lambda t)$ and substituting into eqn. (2), we obtain the secular determinant and then the characteristic equation:

$$\lambda^3 - \alpha\lambda^2 + \beta\lambda - \gamma = 0$$

where:

$$\alpha = a_1, \beta = a_3 + w^2, \gamma = a_2 \text{ (see previous section)}$$

This equation is best solved by computer. The solution of the system (2) is given by:

$$A(t) = \sum_{i=1}^3 A_{i0} e^{-\lambda_i t}$$

$$B(t) = \sum_{i=1}^3 B_{i0} e^{-\lambda_i t}$$

$$C(t) = \sum_{i=1}^3 C_{i0} e^{-\lambda_i t}$$

For the determination of the coefficients the boundary conditions $A(0) = 1$ and $B(0) = C(0) = 0$ are used. By substituting these equations into the homogeneous system (2) a set of boundary conditions is obtained for the first derivatives and hence by a similar procedure the boundary conditions for the second derivatives. The equations for the coefficients A_{i0} are then:

$$A_{10} + A_{20} + A_{30} = 1$$

$$\lambda_1 A_{10} + \lambda_2 A_{20} + \lambda_3 A_{30} = n + k_1$$

$$\lambda_1^2 A_{10} + \lambda_2^2 A_{20} + \lambda_3^2 A_{30} = (n + k_1)^2 + k_1 k_2$$

It follows from the well-known procedure that:

$$A_{10} = \frac{D_{10}}{D} = \frac{1}{D} \{ \lambda_3^2 (\lambda_2 - n - k_1) - \lambda_2^2 (\lambda_3 - n - k_1) - [(n + k_1)^2 + k_1 k_2] (\lambda_2 - \lambda_3) \}$$

$$A_{20} = \frac{D_{20}}{D} = \frac{1}{D} \{ \lambda_1^2 (\lambda_3 - n - k_1) - \lambda_3^2 (\lambda_1 - n - k_1) - [(n + k_1)^2 + k_1 k_2] (\lambda_3 - \lambda_1) \}$$

$$A_{30} = \frac{D_{30}}{D} = \frac{1}{D} \{ \lambda_2^2 (\lambda_1 - n - k_1) - \lambda_1^2 (\lambda_2 - n - k_1) - [(n + k_1)^2 + k_1 k_2] (\lambda_1 - \lambda_2) \}$$

where:

$$D = \lambda_1^2(\lambda_3 - \lambda_2) + \lambda_2^2(\lambda_1 - \lambda_3) + \lambda_3^2(\lambda_2 - \lambda_1)$$

with corresponding expressions for B and C :

$$B_{10} = \frac{D'_{10}}{D} = \frac{k_1}{D} [\lambda_3^2 - \lambda_2^2 - (n + n' + k_1 + k_2 + k_3)(\lambda_3 - \lambda_2)]$$

$$B_{20} = \frac{D'_{20}}{D} = \frac{k_1}{D} [\lambda_1^2 - \lambda_3^2 - (n + n' + k_1 + k_2 + k_3)(\lambda_1 - \lambda_3)]$$

$$B_{30} = \frac{D'_{30}}{D} = \frac{k_1}{D} [\lambda_2^2 - \lambda_1^2 - (n + n' + k_1 + k_2 + k_3)(\lambda_2 - \lambda_1)]$$

$$C_{10} = \frac{D''_{10}}{D} = \frac{k_1 k_3}{D} (\lambda_3 - \lambda_2)$$

$$C_{20} = \frac{D''_{20}}{D} = \frac{k_1 k_3}{D} (\lambda_1 - \lambda_3)$$

$$C_{30} = \frac{D''_{30}}{D} = \frac{k_1 k_3}{D} (\lambda_2 - \lambda_1)$$

If, however, the decay of the concentrations of the excited states is distorted by the finite time of excitation, the solution of system (2) is no longer sufficient. Mathematically this is treated by the convolution integral:

$$A'(t) = \int_0^t A(\theta) I(t - \theta) d\theta$$

where $A(t)$ is the solution of the system (2) and $A'(t)$ the measured signal. A critical survey of the determination of the system parameters by using this integral is given by Knight and Selinger [7] and by Shaver and Love [8].

For the fluorescence transformation of 1-naphthol we obtain the following results (the units are 10^9 s^{-1} or $10^9 \text{ M}^{-1} \text{ s}^{-1}$):

$$n = 0.02 \quad n' = 4 \quad n'' = 0.125$$

$$k_1 = 7 \quad k_2 \ll 1 \quad k_3 = 10 \quad k_4 = 93$$

In the general case, the evaluation of the rate constants requires the use of all three types of disturbance or excitation accompanied by computer analysis by simulation or the regression method.

References

- 1 A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 1961.
- 2 *Techniques of Chemistry*, Vol. VI: Investigation of Rates and Mechanisms of Reactions, Part I, S. Lewis (ed.); Part II, G. G. Hammes (ed.), Wiley, New York, 1975.

- 3 Ch. Kühne and A. Walter, *Z. Phys. Chem. (Leipzig)*, 256 (1975) 487, 689.
- 4 E. Vander Donckt and G. Porter, *Trans. Faraday Soc.*, 64 (1968) 3215, 3218.
- 5 S. G. Schulman and P. Liedke, *Z. Phys. Chem. (N.F.)*, 84 (1973) 317.
- 6 G. Heidt and R. Matysek, to be published.
- 7 A. E. W. Knight and B. Selinger, *Spectrochim. Acta*, 27a (1971) 1223.
- 8 L. A. Shaver and L. J. Cline Love, *Appl. Spectros.*, 29 (1975) 485.