

KINETICS OF PHOTOCHEMICAL REACTIONS WITH EXCITATION BY POLYCHROMATIC RADIATION

Radim HRDINA, Igor ČEPČIANSKY and Jaroslav POSKOČIL

*Department of Technology of Organic Compounds,
Institute of Chemical Technology, 532 10 Pardubice*

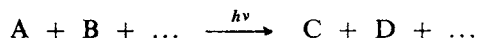
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For quantitative studies of photochemical reactions with low quantum yields the paper suggests application of polychromatic radiation sources whose overall intensity is by orders higher than that of currently available monochromatic sources. The more complicated and laborious calculation methods suggested for treatment of the experimental data can be solved by usual numerical procedures.

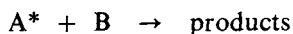
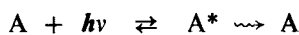
Kinetic studies of photochemical reactions are often difficult because of very low quantum yields of the reactions examined, so that experimental reasons make it necessary to use high-intensity radiation. As there are only few sources producing monochromatic radiation of suitable wavelength¹, monochromatic radiation is usually obtained by separation from polychromatic radiation by application of absorption filters or monochromators². Such separation, however, lowers the intensity of incident radiation by orders of magnitude, and kinetics of photochemical reactions with quantum yields of 10^{-4} to 10^{-5} order of magnitude becomes highly time-consuming.

Application of computers offers a possibility to study the kinetics of photochemical reactions with excitation by polychromatic radiation whose non-reduced intensity ensures a sufficiently rapid course of the reaction. Kinetics of photochemical reactions with participation of monochromatic radiation is described relatively well in available literature. However, the mathematical apparatus and methods of quantitative study of photochemical reactions using polychromatic radiations have not been developed so far.

Let us consider a photochemical reaction



In this schematic equation, *e.g.*, A represents the photochemically active substance, *i.e.*, the excited state A* is responsible for the proper reaction course:



If, in this system², monochromatic radiation of the wavenumber $\bar{\nu}$ impinges perpendicularly into the solution through the front wall of the cell, then the reaction rate (e.g. decrease of compound A) is given by the following equation:

$$r_v = -\frac{d[A]}{dt} = \frac{S}{V} \phi I T_f \frac{E_A}{E} (1 - 10^{-IE}), \quad (1)$$

$$E_A = \varepsilon_A [A], \quad (2)$$

$$E = \sum_i \varepsilon_i [X_i], \quad (3)$$

where the variables r_v (the reaction rate [$\text{mol l}^{-1} \text{s}^{-1}$]), ϕ (quantum yield of the reaction), I (the radiation intensity incident in the solution – in photons [$\text{mol s}^{-1} \cdot \text{cm}^{-2}$]), T_f (transmissivity of the filter used), ε_A (decadic molar absorption coefficient of compound A [$\text{l mol}^{-1} \text{cm}^{-1}$]), and ε_i (decadic molar absorption coefficient of compound X_i [$\text{l mol}^{-1} \text{cm}^{-1}$]) are functions of wavenumber ν , whereas the variables S (the irradiated area of the cell [cm^2]), V (volume of the solution in the cell [cm^3]), l (the optical path of the cell [cm]), and $[A]$, $[X_i]$ (actual concentrations of compounds A and X_i , resp. [mol l^{-1}]) are independent of the wavenumber.

The E values of Eq. (3) are obtained by summation involving all compounds absorbing at the given wavenumber ν_i (inclusive of compound A and solvent).

If the whole front wall of the cell is irradiated, it is

$$r = \frac{1}{l} \phi I T_f \frac{E_A}{E} (1 - 10^{-IE}). \quad (4)$$

As available sources of monochromatic radiation produce low radiation intensities, polychromatic radiation is used instead. The overall reaction rate observed in the experimental cell will then be equal to integral sum of the individual rates:

$$r = \int r_v d\nu = \frac{1}{l(\bar{\nu}_m - \bar{\nu}_n)} \int_{\bar{\nu}_n}^{\bar{\nu}_m} \phi I T_f \frac{E_A}{E} (1 - 10^{-IE}) d\bar{\nu}, \quad (5)$$

where $\bar{\nu}_m$, $\bar{\nu}_n$ represent the upper and the lower limits of wavenumbers of the polychromatic radiation beam emitted by the source. These are constants for a given source.

As the integral (5) cannot be solved analytically, we will make use of knowledge of discrete values of variables in the integral – *i.e.* I_i , $T_{f,i}$, $E_{A,i}$, E_i at the wavenumbers $\bar{\nu}_i$ – and replace the integral by the summation (6) (numerical integration).

$$r = \frac{1}{I(\bar{\nu}_m - \bar{\nu}_n)} \sum_i \varphi_i I_i T_{f,i} \frac{E_{A,i}}{E_i} (1 - 10^{-IE_i}) \Delta\bar{\nu}, \quad (6)$$

where $\Delta\bar{\nu}$ means the integration step

$$\Delta\bar{\nu} = \bar{\nu}_{i+1} - \bar{\nu}_i. \quad (7)$$

Knowing the I_i intensities at the wavenumbers ν_i , we can use Eq. (6) for calculation of the unknown quantum yields (φ_i)*.

In numerical solution of Eq. (5) it is possible to calculate the quantum yields as unknown parameters. Due to computational reasons (number of the φ_i parameters or formation of a singular matrix) it is impossible to calculate the quantum yields φ_i for every wave number $\bar{\nu}_i$ (the numerical integration (6) over the whole range of spectrum of the source can involve up to several thousands of steps i).

Therefore, it will be presumed that there are uniform quantum yields for individual types of electronic transitions (*e.g.* $\Phi(n \rightarrow \pi^*)$, $\Phi(\pi \rightarrow \pi^*)$) which represent a kind of mean quantum yields of the given absorption bands³.

Therefrom it follows that, within the range of wavenumbers of the given absorption band of compound A, the quantum yield will not be a function of the wavenumber but will be constant (8).

$$\Phi = \frac{\sum_{i=1}^n \varphi_i}{n} \quad (8)$$

In the usual case in which only one excited state is photochemically active (*i.e.* only photons absorbed by one absorption band are responsible for the photochemical reaction) it will be:

$$r = \frac{1}{I(\bar{\nu}_m - \bar{\nu}_n)} \Phi \sum_{i=1}^n I_i T_{f,i} \frac{E_{A,i}}{E_i} (1 - 10^{-IE_i}) \Delta\bar{\nu}, \quad (9)$$

where again $\Delta\bar{\nu}$ means the integration step

$$\Delta\bar{\nu} = (\bar{\nu}_p - \bar{\nu}_k)/n, \quad (10)$$

* If we know quantum yields φ_i of a certain reaction (chemical actinometers), we can use Eq. (6) for calibration of the radiation incident into the solution (determination of I_i).

the wavenumbers $\bar{\nu}_p, \bar{\nu}_k$ limiting the given active absorption band of compound A. Thereby the calculation is reduced to optimization of one Φ parameter only.

If there are several active absorption bands (the j index), the reaction rate will be

$$r = \frac{1}{l(\bar{\nu}_m - \bar{\nu}_n)} \sum_{j=1}^k \Phi_j \sum_{i=n_j}^{m_j} I_i T_{r,i} \frac{E_{A,i}}{E_i} (1 - 10^{-IE_i}) \Delta\bar{\nu}, \quad (11)$$

the number of unknown parameters (quantum yields Φ) being k .

Several conditions must be fulfilled for successful solution of the the kinetic relation (11). First we must precisely know the values of radiation intensities incident into the solution (in mol of photons per second per cm^2 in dependence on wavenumber⁴). The second conditions follows from emission characteristics of available radiation sources whose spectrum usually has line character combined with a certain emission continuum¹. As the width of emission lines is not usually large, the integration step chosen must be relatively small: so *e.g.* for the HBO 200 (Narva) discharge lamp a sufficient integration step was about 5 cm^{-1} . Therefrom it follows that the number of integration steps will be of 10^3 order of magnitude. Solution of this problem necessitates then application of a computer with relatively large memory capacity. (A program for calculation of intensities of radiation absorbed by the components for use in solution of kinetic problems is available in our Department).

Many photochemical reactions exhibit a rate directly proportional to the radiation amount absorbed by a ceratin compound, the other components acting as an inner filter. There exist cases, however, in which the reaction rate is generally given by a power of the radiation absorbed by the given component (radical chain reactions), or it is even necessary to know (for solution of certain kinetic problems) also the amounts of photons absorbed by several components. In any case the basic task consists in estimation of the amount of photons absorbed by the individual components in the course of the whole reaction (in accordance with time changes of concentrations of the individual components).

$$I_x = \frac{1}{l(\bar{\nu}_m - \bar{\nu}_n)} \sum_{i=1}^n I_i T_{r,i} \frac{E_{x,i}}{E_i} (1 - 10^{-IE_i}) \Delta\bar{\nu}, \quad (12)$$

where I_x stands for the amount of photons absorbed by the X component with actual concentration $[X]$ at the time t [$\text{mol s}^{-1} \text{ l}^{-1}$]. And here we come to the basic problem and condition of solution of Eqs (11) and (12): we must know concentrations of all participants (for calculation of E – see Eq. (3)) during the whole course of the photochemical reaction. This is because only rarely cases are encountered in which spectra of the individual participants do not overlap. Estimation of actual concentrations of the individual compounds throughout the reaction represents a big problem by

itself. If the reaction involves reactive intermediates (radicals, excited molecules, *etc.*), then the problem only can be solved with application of the Bodenstein steady state treatment, *i.e.* with the presumption that their concentrations are constant and very low (as compared with the other compounds) and, hence, their adsorbance can be neglected.

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