

THEORETICAL MODELS FOR PHOTOCATALYSIS PROCESS

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1. INTRODUCTION

Regulation of charge transfer processes in chemical systems is the basis for obtaining of one or another end product. At the same time, big possibilities occur during regulation of the chemical processes when influencing on a system by external factors. Particularly, influence by the photons of defined energy allows realization of such complex chemical transformations in the system and obtaining of such products, receive of which is impossible in other conditions. Photo-catalysis has been used for a long time, theoretical fundamentals for photo-catalysis mechanisms have been also worked out long ago¹⁻⁷.

Modern theory of charge transfer processes in nonregular condensed systems increases substantially capabilities of conduction of analytic calculations of kinetic parameters of the processes, particularly for photo-catalysis processes.

Theoretical basis of charge photo-transfer processes in chemical systems will be considered below. The analysis of analytic expressions for kinetic parameters, particularly, for the rate constant of the process, will allow to identify those ranges of parameters' values, when photo-transfer process passes catalytically.

2. Model Hamiltonian

We consider model system, which is condensed medium with dissolved reagents. Concentration of the particles-reagents is supposed sufficiently low, in order to neglect direct interaction of one type of the reagents with each other and to consider interaction of the group of the particles, which brings to reaction. It is assumed also, that photon flux acts upon the system. Adsorption of one photon brings to one act of charge photo-transfer with obtaining of reaction products.

Electron-nonadiabatic processes of direct outer-sphere photo-transfer processes are considered for concreteness.

It is assumed generally, that interaction of reagents with the medium has either weak character or is such strong, that reagents form complexes and just these complexes are considered as reagents. At the same time, in amorphous solid media polarizable particles, placed in condensed medium, can form intermediate bond with medium. They are partially polarized and their frequency spectra and geometric structure are different than in gaseous phase at that.

We consider charge transfer processes [8] between dipole-active (in general form) polarizable (electron and infra-red polarization) particles in irregular condensed medium when polarization and fluctuation mechanism of interaction of reagents with medium is taken into account [9].

System's Hamiltonian is represented in the form:

$$H = H_m + H_p + H_{ph} + H_{int}^{ph} + H_{int} + F_s + H_{int}^{(1)} + H_{int}^{(2)}$$

Here H_m is Hamiltonian of polarized medium, H_{ph} is Hamiltonian of phonons, H_{int}^{ph} is Hamiltonian of interaction of reagents with the field of photons, H_{int} is Hamiltonian of interaction of condensed medium with the reagents' electromagnetic field:

$$H_{int} = -\int \vec{P}(\vec{r}) \vec{E}(\vec{r}) d\vec{r}$$

(\vec{E} is tension of electromagnetic field transverse photons), F_s is polarization energy of reagents, $H_{\text{int}}^{(1)}$ and $H_{\text{int}}^{(2)}$ are Hamiltonians of interaction of polarization fluctuations $\delta\vec{P}$ of medium with static field of reagent and intra-molecular vibrations of reagent correspondingly:

$$H_{\text{int}}^{(1)} = \int \delta\vec{P}\vec{E}_0 dV; H_{\text{int}}^{(2)} = \int \delta\vec{P}\vec{v}Q dV; \vec{v} = \frac{\partial\vec{E}_0}{\partial Q}$$

H_p - is Hamiltonian of polarized reagents (for short is adduced in operator form):

$$H_p = H_p^0 + \sum_n d_n^{i,f} Q_n^{i,f} + \sum_{nm} h_{nm}^{if} Q_n^{i,f} Q_{nm}^{if};$$

$$d_n^{i,f} = \frac{1}{2} (E_0^{i,f} G_{pp} \frac{\partial E_0}{\partial Q_n} + \frac{\partial E_0}{\partial Q_n} G_{pp} E_0^{i,f});$$

$$h_{nm}^2 = -\frac{1}{2} \frac{\partial E_0}{\partial Q_n} G_{pp} \frac{\partial E_0}{\partial Q_m}$$

where H_p^0 is Hamiltonian of the reagents in vacuum, E_0 is tension of electric field of reagents, G_{pp} is Green's function of polarization operators of medium, Q_n are normal coordinates of intra-molecular vibrations of reagents.

h_{nm}^2 - may be of sufficiently great value, so that the frequency of some intramolecular vibration may be considerably less than its value in vacuum.

Green function G_{pp} has the form [10]:

$$G_{p_\alpha p_\beta}(\vec{r}, \vec{r}'; \tau - \tau') = -\langle T_\tau P_\alpha(\vec{r}, \tau) P_\beta(\vec{r}', \tau') \rangle_0$$

where angle brackets mean quantum-statistical averaging according to states of Hamiltonian of condensed system, $\vec{P}(\vec{r})$ is polarization operator of condensed medium, τ - "imaginary time".

Formula (2) allows calculation of vibrational spectrum and lengths of chemical bonds of polarized reagent, which is placed in condensed medium.

Energy of polarization of particle has the form:

$$F_s = \frac{1}{2} \int d\vec{r} d\vec{r}' E_\alpha^0(\vec{r}) G_{p_\alpha p_\beta}^R(\vec{r}, \vec{r}'; \omega = 0) E_\beta^0(\vec{r}')$$

where $G_{p_\alpha p_\beta}^R(\vec{r}, \vec{r}'; \omega = 0)$ is retarded Green function of polarization operators at zero frequency.

Interaction Hamiltonian of reagents and medium molecules with transverse photons' field H_{int}^{ph} can be represent in the form:

$$H_{\text{int}}^{ph} = -\int \vec{P}^r(\vec{r}) \vec{E}^{ph}(\vec{r}) d\vec{r}$$

Where \vec{P}^r is polarization operator of the reagents; \vec{E}^{ph} is operator of intensity of photon's filed. Hamiltonian of final state has the form analogous to the first formula with the difference that in the final state is one photon energy h ν .

4. Rate constant of the charge photo-transfer process

Probability of electron transfer process with participation of photon has the form:

$$dW = \sum_{n(N_{\vec{k}\sigma})} \sum_{n'(N_{\vec{k}'\sigma})} e^{\beta(F_i - F_{fn})} \phi_i(N_{\vec{k}\sigma}) 2\pi \left| \langle (N_{\vec{k}\sigma}) n' | L_{fi} | (N_{\vec{k}\sigma}), n \rangle \right|^2 \delta(E_{in} - E_{fn'} + \sum_{\vec{k}\sigma} \omega_k (N_{\vec{k}\sigma} - N_{\vec{k}'\sigma}))$$

$(N_{\vec{k}\sigma})$ is occupation number of photons; $\phi_i(N_{\vec{k}\sigma})$ is function of photon distribution in initial state; F_i is free energy of system in initial state; $E_{in}, E_{fn'}$ are energy spectra of the system in initial and final states; L_{fi} is matrix element of interaction Hamiltonian.

\vec{E} is operator of intensity of photon field, which can be represented as:

$$\vec{E}(\vec{r}) = i \sum_{\vec{k}\sigma} \left(\frac{2\pi\omega_k}{V} \right)^{1/2} \vec{e}_{\vec{k}\sigma} (a_{\vec{k}\sigma} e^{i\vec{k}\vec{r}} - a_{\vec{k}\sigma}^+ e^{-i\vec{k}\vec{r}})$$

where $a_{\vec{k}\sigma}^+, a$ are operators of birth and annihilation of photons, $\vec{e}_{\vec{k}\sigma}$ - is vector of photons polarization, V - volume of the system.

After simple transformation we'll obtain

$$dW = \frac{\beta}{i} \int_{C_0} d\theta \int d\vec{r} d\vec{r}' \langle E_\beta(\vec{r}', \theta) E_\alpha(\vec{r}, 0) \rangle_i \langle e^{\beta\theta H_i} P_\beta^*(\vec{r}')_{fi} e^{-\beta\theta H_f} P_\alpha(\vec{r})_{fi} \rangle_i$$

where H_i is Hamiltonian of system in the initial state, H_f is system Hamiltonian in the final state. It is assumed, that there are sufficiently many photons in the system and both processes may be realized - as processes with absorption, so processes with radiation of photon.

$$E_\beta(\vec{r}'; \theta) = e^{\beta\theta H_f} E(\vec{r}; \theta = 0) e^{-\beta\theta H_i},$$

$$\langle E_\beta(\vec{r}'; \theta) E_\alpha(\vec{r}, 0) \rangle = \sum_{\vec{k}\sigma} \frac{2\pi\omega_k}{V} e_{\vec{k}\sigma}^\alpha e_{\vec{k}\sigma}^\beta \left\{ \left(1 + \langle N_{\vec{k}\sigma} \rangle_i \right) e^{-\beta\theta\omega_k} e^{ik(\vec{r}' - \vec{r})} + \langle N_{\vec{k}\sigma} \rangle_i e^{\beta\theta\omega_k} e^{-ik(\vec{r}' - \vec{r})} \right\}$$

Calculation of probability of charge transfer process with radiation and absorption of photons may be conducted in general form in the same model approximations, which are for thermal processes of electron transfer.

It is assumed that number of vibrational degrees of freedom in the beginning and at the end of the process is equal. Even at this assumption general expression for rate constant has rather bulky character. For simplicity we'll be restricted with the case when intramolecular oscillations may be considered as classical.

Rate constant of phototransfer process can be expressed as:

$$K = \sum_{\sigma=1}^2 \frac{|L_{fi}^\sigma(\vec{R}^*, \Psi^*)|^2}{\sqrt{|\Psi_{\theta\theta}''|}} \phi^\sigma \Phi(\vec{R}^*, \Psi^*) U(\vec{R}^*, \Psi^*) \exp \left\{ -\beta\theta^* (\Delta F - \hbar\omega^\sigma) - \Psi^m(\vec{R}^*, \Psi^*; \theta) - \beta \sum_{n=1}^N E_m \frac{\theta^* (1 - \theta^*) \omega_n^i \omega_n^f}{(1 - \theta^*) (\omega_n^i)^2 + \theta^* (\omega_n^f)^2} - \theta^* \sum_{k=1}^N \ln(\omega_k^f / \omega_k^i) - \theta^* \ln \left[1 + \beta \sum_{k=1}^N (G_k(\vec{R}^*, \Psi^*) + \frac{\omega_k^f}{\omega_k^i} \overline{G}_k(\vec{R}^*, \Psi^*)) \frac{\sqrt{2E_{rk} \omega_k^i}}{\omega_k^f} \right] \right\} (2\pi)^{1/2} \left[\prod_{s=1}^N \frac{\omega_s^i}{\sqrt{(1 - \theta^*) (\omega_s^i)^2 + \theta^* (\omega_s^f)^2}} \right] \left\{ 1 + \sum_{k=1}^N \left[G_k(\vec{R}^*, \Psi^*) + \frac{\omega_k^f}{\omega_k^i} \overline{G}_k(\vec{R}^*, \Psi^*) \right] (\beta\theta^* - F_{\omega}(\theta^*)) \sqrt{2E_{rk} \omega_k^i \theta^* (\omega_k^f)^2} \left[(1 - \theta^*) (\omega_k^i)^2 + \theta^* (\omega_k^f)^2 \right]^{3/2} \right\};$$

Where ϕ^σ is the distribution function of the photons; the values of the coordinates of the reagents \vec{R}^* and the angles of their orientation ψ^* in the transitional configuration; Brensted factor of symmetry θ^* depends on photon polarization σ , the quantity $1/\sqrt{|\psi''_{\theta\theta}|}$ is width of integral over θ , and point of inflection θ^* may be found from equation:

$$\beta(\Delta F - h\nu) + \frac{\partial \Psi^m(\vec{R}^*, \psi^*; \theta)}{\partial \theta} + \frac{\partial}{\partial \theta} \sum_{k=1}^N \beta E_{rk} \frac{\theta(1-\theta)\omega_k^i \omega_k^f}{(1-\theta)(\omega_k^i)^2 + \theta(\omega_k^f)^2} + \ln \prod_{k=1}^N \frac{\omega_k^f}{\omega_k^i} + \ln \left\{ 1 + \beta \sum_{k=1}^N \left[G_k(\vec{R}^*, \psi^*) + \frac{\omega_k^f}{\omega_k^i} \bar{G}_k(\vec{R}^*, \psi^*) \right] \frac{\sqrt{2E_{rk} \omega_k^i}}{\omega_k^f} \right\} = 0$$

In these formulas L_{fi} is resonance integral of interaction of reagents (some particle or group of particles) with photons (dipole moment of charge phototransfer). Matrix element is calculated with use of wave functions in frames of concrete model for reagents. Resonance integral L_{fi} can be considered as some phenomenological parameter. Arguments of this resonance integral characterize geometric characteristics of the process, distance between particles, spatial orientation of the particle. Function $\Phi(\vec{R}^*, \psi^*)$ is distribution function of reagents. Model function may be selected as this function. For homogeneous systems particle distribution function has most simple form.

$\Psi^m(\vec{R}^*, \psi^*; \theta)$ is function of medium reorganization. Its formal expression is:

$$\Psi^m(\vec{R}^*, \psi^*, \theta) = \frac{1}{\pi} \int d\vec{r} d\vec{r}' \Delta E_i(\vec{r}; \vec{R}^*, \psi^*) \Delta E_k(\vec{r}'; \vec{R}^*, \psi^*) \int_{-\infty}^{\infty} d\omega \operatorname{Im} g_{ik}^R(\vec{r}, \vec{r}'; \omega) \frac{\operatorname{sh} \frac{\beta\omega(1-\theta)}{2} \operatorname{sh} \frac{\beta\omega\theta}{2}}{\omega^2 \operatorname{sh} \frac{\beta\omega}{2}}$$

For charge transfer processes medium reorganization energy is determined by formula:

$$E_r^m(\vec{R}, \psi) = -\frac{1}{2} \int d\vec{r} d\vec{r}' \Delta E_i(\vec{r}; \vec{R}, \psi) g_{ik}^R(\vec{r}, \vec{r}'; \omega = 0) \Delta E_k(\vec{r}'; \vec{R}, \psi)$$

Here $\Delta E_i(\vec{r}; \vec{R}, \psi)$ is change of system's electrostatic field strength during transfer process and Green function g^R is temporal function of polarization fluctuations operators of amorphous solid and liquid at finite temperature. In factorization approximation for function g^R we have:

$$g_{ik}^R(\vec{r}, \vec{r}'; \omega) = g_{ik}^R(\vec{r}, \vec{r}'; \omega = 0) f(\omega).$$

Reorganization function of medium can be expressed as:

$$\Psi^m(\vec{R}^*, \psi^*, \theta) = E_r^m \frac{2}{\hbar} \int_{-\infty}^{\infty} d\omega f(\omega) \frac{\operatorname{sh} \frac{\beta\omega(1-\theta)}{2} \operatorname{sh} \frac{\beta\omega\theta}{2}}{\omega^2 \operatorname{sh} \frac{\beta\omega}{2}}$$

When taking integrals over r and r' it is necessary to consider geometry of channel and the circumstance, that as effects of spatial dispersion of medium (function $g(r, r')$), so effects of frequency dispersion (function $F(\omega)$) must be described by different model functions for amorphous condensed medium.

E_m is reorganization energy of n-th intra-molecular degree of freedom of adsorbing particle [4], and ω is correspondingly frequency of intra-molecular vibration in the beginning and at the end of the process.

Reorganization functions G and \bar{G} are defined from the formulas:

$$G(\bar{R}, \psi) = -\frac{1}{2} \int d\bar{r} d\bar{r}' \frac{\partial E_i}{\partial Q}(\bar{r}; \bar{R}, \psi) g^{R_{ik}}(\bar{r}, \bar{r}'; \omega = 0) \Delta E_k(\bar{r}'; \bar{R}, \psi)$$

$$\bar{G}(\bar{R}, \psi) = -\frac{1}{2} \int d\bar{r} d\bar{r}' \Delta E_i(\bar{r}; \bar{R}, \psi) g^{R_{ik}}(\bar{r}, \bar{r}'; \omega = 0) \frac{\partial E_k}{\partial Q}(\bar{r}'; \bar{R}, \psi)$$

Q is normal coordinate of intra-molecular vibrations of reagents.

Everything that is concerned to medium reorganization must be considered at their calculation. Functions adduced in [4] were used as model functions for description of effects of frequency and spatial dispersion of medium. As conducted calculations have shown, carrying out of analytical calculations to the end is impossible, and it is necessary to conduct numerical integration.

Activation energy E_{ac} of the process is determined by formula:

$$K = \Phi \exp(-\beta E_{ac}),$$

where

$$E_{ac} = \theta^*(1 - \theta^*) E_r^m - (\Delta F - h\nu) \theta^* + \sum_{k=1}^N E_{rk} \theta^* (1 - \theta^*) \omega_k^i \omega_k^f \left[(1 - \theta^*) (\omega_k^i)^2 + \theta^* (\omega_k^f)^2 \right]^{-1} +$$

$$+ kT \theta^* \ln \left[1 + \beta \sum_{k=1}^N \left(G_k + (\omega_k^f / \omega_k^i) \bar{G}_k \right) \right] \left(2E_{rk} \omega_k^i \right)^{1/2} (\omega_k^f)^{-1} + \theta^* \sum_{k=1}^N \ln(\omega_k^f / \omega_k^i)$$

Φ is pre-exponential factor.

Expression of rate constant will be considerably simplified, if we'll neglect interaction of intra-molecular vibrations of the particle with fluctuations of medium polarization:

$$E_{ac} = \theta^*(1 - \theta^*) E_r^m - (\Delta F - h\nu) \theta^* + \sum_{k=1}^N E_{rk} \theta^* (1 - \theta^*) \omega_k^i \omega_k^f \left[(1 - \theta^*) (\omega_k^i)^2 + \theta^* (\omega_k^f)^2 \right]^{-1}$$

Equation for determination of θ^* correspondingly will have the form:

$$\beta(\Delta F - h\nu) + \frac{\partial \psi^m(R^*, \psi^*; \theta)}{\partial \theta} + \frac{\partial}{\partial \theta} \sum_{k=1}^N \beta E_{rk} \frac{\theta(1 - \theta) \omega_k^i \omega_k^f}{(1 - \theta) (\omega_k^i)^2 + \theta (\omega_k^f)^2} = 0$$

If intra-molecular reorganization of particle may be also neglected, then:

$$E_{ac} = \theta^*(1 - \theta^*) E_r^m - (\Delta F - h\nu) \theta^*$$

and for determination of θ^* we have equation:

$$\beta(\Delta F - h\nu) + \frac{\partial \psi^m(R^*, \psi^*; \theta)}{\partial \theta} = 0$$

For convenience of analysis equation for K may be presented in the form:

$$K = \sum_{\sigma}^2 |L_{fi}^{\sigma}|^2 \phi_{\sigma}^v N \exp\{-\beta\theta_{\sigma}^* \Delta F_{\sigma} + h\nu\beta\theta_{\sigma}^* - \psi_{\sigma}^m(\theta_{\sigma}^*) - \psi_{\sigma}^v(\theta_{\sigma}^*) - \psi_{\sigma}^{mv}(\theta_{\sigma}^*)\}$$

Functions $\Psi^v(\bar{R}^*, \psi^*; \theta)$ and $\Psi^{mv}(\bar{R}^*, \psi^*; \theta)$ have rather complex form and are reorganization functions of vibration subsystem. Electron resonance integral $|L_{fi}^{\sigma}(\bar{R}^*, \psi^*)|$ is calculated as non-diagonal matrix element of interaction of reagents with photon by electron wave-functions of initial and final states of the system. Function $N(\bar{R}^*, \psi^*; \theta; \omega_n)$ is calculated for concrete processes with consideration of geometry of the particles. Obtained analytic expressions may be used for finding of analytic expression for optical density of the process.

We use the approach, which is analogous to Lambert-Beer law for optical density D :

$$D = \ln\left(\frac{I_0}{I}\right) = \kappa d$$

where I_0 is intensity of light on input of the measurement cell with thickness d , I is intensity of light on output of the cell. Proportionality coefficient κ may be substituted for extinction coefficients of particles adsorption ε_a and extinction coefficient of the direct outersphere transition of the system with photon adsorption ε_{ab} :

$$\kappa = \sum_a C_a \varepsilon_a + \sum_{ab} C_a C_b \varepsilon_{ab} + \dots$$

where C_a is concentration of a-type particles.

More extensive information may be obtained from the form of absorption curve of photon radiation by the system as function of photon energy $h\nu$. In case of implementation of extinction coefficient for photon absorption processes during electron transfer process between reagents, the following expression will be obtained:

$$\varepsilon = h\nu |L_{fi}^{\sigma}|^2 \phi^v A^v \exp\{-\beta\theta^* \Delta F + h\nu\beta\theta_{\sigma}^* - \psi^m(\theta^*) - \psi^v(\theta^*) - \psi^{mv}(\theta^*)\}$$

Cited above formulas considerably simplify for the models, where interaction of intramolecular vibrations with fluctuations of polarization of condensed medium is not taken into account.

Application of this correlation allows realization of analysis for wide range of processes. It is necessary to select concrete model for that, in the framework of this model to simplify analytically general expressions and from comparison with experimental data to obtain numerical values of reorganization energies, transfer dipole moment, reorganization of quantum subsystem etc.

In case when distribution function of reagents is known, the last correlation allows calculation of dipole moment of transfer and correspondingly evaluation of transfer interval being rather substantial during investigation of complicated systems.

CONCLUSION

During photolysis, substance subject to decomposition is irradiated by light of specified wave length, which must correspond or be near to maximum of light absorption by the substance. Under influence of such irradiation vibration of atoms in molecule become stronger, stimulating bond breakage between them. For example, for molecule of hydrogen sulfide such wave lengths are in the interval of wave lengths of mercury lamp emission spectrum (250-600 nm), at that, most intensive line in this spectrum (254 nm) has wave length near to vibration frequency of hydrogen atoms in molecule H_2S . Selection of corresponding modified zeolite will allow realization of hydrogen sulfide, methane, etc., photolysis process more economically.

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