Simultaneously occurring spontaneous and photochemical redox reactions of complexes
Determination of kinetic data

J. ŠIMA and D. VALIGURA

Department of Inorganic Chemistry, Slovak Technical University,
880 37 Bratislava

The paper presents a model for studying the kinetics of simultaneously occurring spontaneous and photochemical redox reactions of complexes. Conditions of the general and concrete applications of this model for study of redox processes of halogeno complexes of Fe(II) and Fe(III) are discussed.

В работе приводится модель для изучения кинетики одновременно протекающих самопроизвольных и фотохимических окислительно-восстановительных реакций комплексных соединений. Обсуждаются возможности применимости этой модели вообще и в частности при изучении окислительно-восстановительных процессов галогенокомплексов Fe(II) и Fe(III).

During irradiation of the systems of chloro and bromo complexes of Fe(II) and Fe(III) in the mixtures of acetone and methanol several redox processes occur at the same time: photoreduction of Fe(III) to Fe(II) accompanied with the oxidation of methanol [1], spontaneous[a] oxidation of Fe(II) to Fe(III) by acetone due to the mutual influence of ligands [2], as well as the oxidation of Fe(II) to Fe(III) sensitized by the photoexcited Fe(III)* complexes[b] [3, 4]. The rate of reactions or the values of the quantum yields of the products of individual processes are influenced by the system composition.

The aim to evaluate quantitatively the effect of the system composition on the course of individual redox processes has resulted in necessity to find out a method by means of which it would be possible to determine the rate constants and quantum yields of individual processes from the experimentally measurable data, as well as the constants of the Stern—Volmer sensitizing equation [5].
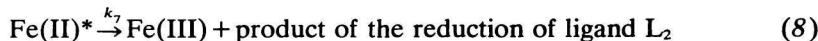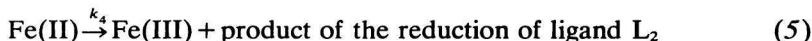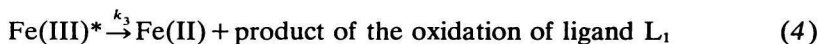
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[a] Instead of "spontaneous reaction" the terms "dark reaction" or "thermal reaction" are used in the literature as well.

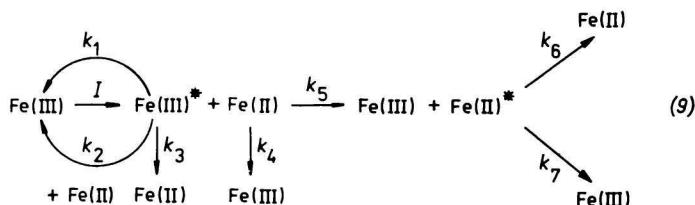[b] Asterisk will denote the particles in electronically excited states.

The model suggested in the paper can be applied to the systems in which radiation is absorbed by the sensitizer only (complexes with the central atom at a higher oxidation state) and in which the sensitizer is the product of a spontaneous and photochemical oxidation of the quencher (complexes with central atom at a lower oxidation state). It is applicable also to the systems of halogeno complexes of Fe(II) and Fe(III) studied in [1—4].

Results and discussion

The processes occurring in the irradiated systems of halogeno complexes of Fe(II) and Fe(III) can be expressed by the reactions as follows

$$\text{Fe(III)} \xrightarrow{h\nu} \text{Fe(III)*} \tag{1}$$

$$\text{Fe(III)*} \xrightarrow{k_1} \text{Fe(III)} \tag{2}$$

$$\text{Fe(III)*} + \text{Fe(II)} \xrightarrow{k_2} \text{Fe(III)} + \text{Fe(II)} \tag{3}$$

$$\text{Fe(III)*} \xrightarrow{k_3} \text{Fe(II)} + \text{product of the oxidation of ligand } L_1 \tag{4}$$

$$\text{Fe(II)} \xrightarrow{k_4} \text{Fe(III)} + \text{product of the reduction of ligand } L_2 \tag{5}$$

$$\text{Fe(III)*} + \text{Fe(II)} \xrightarrow{k_5} \text{Fe(III)} + \text{Fe(II)*} \tag{6}$$

$$\text{Fe(II)*} \xrightarrow{k_6} \text{Fe(II)} \tag{7}$$

$$\text{Fe(II)*} \xrightarrow{k_7} \text{Fe(III)} + \text{product of the reduction of ligand } L_2 \tag{8}$$

or by the scheme

$$\tag{9}$$

where Fe(II) and Fe(III) are complexes of Fe(II) and Fe(III), I is the light flux of radiation absorbed by Fe(III) complexes, k_1 through k_7 are rate constants of individual processes.

In the following paragraphs the Fe(III) concentration will be denoted S (sensitizer), the Fe(II) concentration as Q (quencher in the sensitized processes).

The quantity of radiation I absorbed by the system is given by the following relation

$$I = I_0(1 - 10^{-\varepsilon l S}) \tag{10}$$

where I_0 is the intensity of incident light of a certain wavelength λ, ε is a molar absorption coefficient at given λ, l is the cell length with irradiated system.

Using eqns (1—8), the dependence of the change of S on the time can be derived

$$\frac{dS}{dt} = k_4 Q^n + I_0(1 - 10^{-\varepsilon l S}) \left\{ \frac{k_5 k_7 Q - k_3(k_6 + k_7)}{[(k_1 + k_3) + (k_2 + k_5)Q](k_6 + k_7)} \right\} \tag{11}$$

(provided that the relations for stationary state are used); it is possible to derive from these equations also the dependence of the value of the absorbance A of the systems in the region in which the light is absorbed only by the Fe(III) complexes.

The relation

$$\frac{dA}{dt} = \varepsilon l \frac{dS}{dt} \tag{12}$$

is valid for the systems in which there is an equilibrium between several complexes, this being unchanged with time. The systems studied in [1—4] fulfil this condition within a certain range of S.

The value k_4 and the order of the reaction of spontaneous oxidation n in relation (11) can be defined by following the spontaneous changes in the systems of the Fe(II) complexes.

The difference of experimentally measured dependences of S on time in irradiated and nonirradiated systems expresses changes of S with time as a result of photochemical reactions only and we shall be discussing only these processes.

By following the dependence of S or A on time and by measuring I it is possible to calculate the quantum yields of the photosensitized oxidation of Fe(II) to Fe(III), Φ_{exp} (the rate of oxidation of Fe(II) to Fe(III) was higher in the case of the irradiated systems of halogeno complexes of Fe(II) and Fe(III) than the rate of spontaneous oxidation of Fe(II) to Fe(III)). The quantum yields Φ_{exp} involve also the change of S with time due to photoreduction of Fe(III) to Fe(II) (eqn (4)). In such a case the Stern—Volmer equation has a nonlinear form

$$\frac{1}{\Phi_{exp}} = \frac{(k_1 + k_3) + (k_2 + k_5)Q}{k_5 \eta Q - k_3} \tag{13}$$

where η is given by the following relation

$$\eta = \frac{k_7}{k_6 + k_7} \qquad (14)$$

and expresses the quantum yield of deactivation of Fe(II)* complexes by the redox process.

The theoretical quantum yield of only photosensitized oxidation of Fe(II) to Fe(III), Φ_{theor}, is higher than Φ_{exp} as the change of S with time found experimentally, is lower due to reaction (4) than the change of S with time due to photosensitized processes only. The Stern—Volmer equation in such a case has the form as follows

$$\frac{1}{\Phi_{theor}} = \frac{k_2 + k_5}{k_5 \eta} + \frac{k_1 + k_3}{k_5 \eta Q} \qquad (15)$$

By comparing the relations (13) and (15) it is quite obvious that the difference between Φ_{exp} and Φ_{theor} is given as follows

$$\Phi_{theor} - \Phi_{exp} = \frac{k_3}{(k_1 + k_3) + (k_2 + k_5)Q} = \Phi_{Fe(II)} \qquad (16)$$

where $\Phi_{Fe(II)}$ is the quantum yield of the reaction of the photoreduction of Fe(III) to Fe(II). Both Φ_{theor} and Φ_{exp} depend on time as Q changes with time except the special case when

$$\frac{dS}{dt} = \frac{dQ}{dt} = 0 \qquad (17)$$

The limiting quantum yield of the reaction of the photosensitized oxidation of Fe(II) to Fe(III), Φ_{lim} does not depend on time

$$\Phi_{lim} = \frac{k_5 \eta}{k_2 + k_5} \qquad (18)$$

Provided that one knows the absolute values of some of the rate constants and their ratios it is possible to solve the problem in general.

Employing pulse methods, irradiating of the systems containing only Fe(III) complexes, it is possible to calculate the sum $(k_1 + k_3)$ on the basis of the Fe(III)* lifetime, by calculating the quantum yield of the photoreduction of Fe(III) to Fe(II), a ratio of the above-mentioned constants can be determined in such systems (not containing Fe(II) complexes) and from these two data the absolute values of k_1 and k_3 can be calculated.

Analogically, by irradiation of Fe(II) complexes the values of k_6, k_7, and η can be calculated provided that the irradiation results in the same excited state as in the case of reaction (6).

Having defined Φ_{lim} from the plotted dependence (13) and by calculation of Φ_{exp} for the system with certain Q, equation for the calculation of the values k_2 and k_5 can be derived

$$k_2 = \frac{(\eta - \Phi_{\text{lim}})[k_1\Phi_{\text{exp}} + k_3(\Phi_{\text{exp}} - 1)]}{\eta Q(\Phi_{\text{lim}} - \Phi_{\text{exp}})} \qquad (19)$$

$$k_5 = \frac{\Phi_{\text{lim}}[k_1\Phi_{\text{exp}} + k_3(\Phi_{\text{exp}} - 1)]}{\eta Q(\Phi_{\text{lim}} - \Phi_{\text{exp}})} \qquad (20)$$

Thus, from the values k_1, k_2, k_3, and k_5 it is possible to calculate the Stern—Volmer constant of sensitization K_{SV} [5]

$$K_{\text{SV}} = \frac{k_2 + k_5}{k_1 + k_3} \qquad (21)$$

which cannot be found exactly by the graphical method because of the nonlinear equation (13).

In the case $k_1 \gg k_3$ eqn (15) or (13) can be reduced

$$\frac{1}{\Phi_{\text{exp}}} = \frac{1}{\Phi_{\text{theor}}} = \frac{k_2 + k_5}{k_5\eta} + \frac{k_1}{k_5\eta Q} \qquad (22)$$

and from graphical presentation of this dependence when η and k_1 are known also the values k_2 and k_5 as well as K_{SV} and Φ_{lim} can be found.

The possibility of the application of this method is conditioned by different electronic absorption spectra of the complexes with the central atom at different oxidation states, by the possibility to find out directly the absolute values of some rate constants and in the case of the systems with equilibrium of the complexes by time independence of the fraction concentrations of individual complexes during redox processes.

References

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