PHOTOCATALYTIC EFFECT OF Fe(III) ON OXIDATION OF TWO-CARBON SUBSTRATES RELATED TO NATURAL WATERS

Sarka KLEMENTOVA[a,]* and Dana M. WAGNEROVA[b]

[a] *Hydrobiological Institute,*
Academy of Sciences of the Czech Republic, 370 05 Ceske Budejovice, The Czech Republic
[b] *Institute of Inorganic Chemistry,*
Academy of Sciences of the Czech Republic, 160 00 Prague 6, The Czech Republic

Received December 30, 1992
Accepted July 21, 1993

The influence of ferric ions on photoinitiated reaction of dioxygen with two carbon organic acids, aldehydes and alcohols related to natural waters was demonstrated. Photocatalytic effect of ferric ions, i.e. photochemical reduction of Fe(III) as the catalyst generating step, has been found to be the common principal of these reactions. The overall quantum yields of the reactions are in the range from 0.3 to 1.2. A mathematical model designed for the mechanism of cyclic generation of catalyst in the singlet substrate oxidation by O_2 was applied to the system glyoxalic acid + Fe(III); a fair agreement between the simulated and experimental kinetic curves was obtained. The experimental rate constant is $4.4 \cdot 10^{-4}$ s $^{-1}$.

Reaction of dioxygen occurring in natural waters are influenced by sun radiation and by transition metal ions. Miles and Brezonic[1] observed that the rate of photochemical oxygen consumption in waters of Florida lakes is proportional to the iron concentration and to the amount of radiation absorbed by humic substances which are the main absorbing species in natural waters.

It is known that a direct reaction between oxygen molecule and a molecule of an organic compound is a spin forbidden process, the ground state of oxygen molecule being a triplet whereas that of the organic compound being generally a singlet. If this reaction is to occur, it is necessary to overcome the spin ban, that is to activate a reaction component either catalytically (by transition metal ions) or photochemically.

During the last decade, studies of the role of transition metal ions in photochemical reactions led to the concept of photocatalytic mechanism[2,3]: In the first step, an inactive catalyst precursor A is transformed photochemically into a catalyst C – Eq. (*1*); in the

---

* Present address: Faculty of Biological Sciences, University of South Bohemia, Branisovska 31, 370 05 Ceske Budejovice, The Czech Republic.

second step, the catalyst C catalyzes a subsequent thermal (non photochemical) reaction of a substrate S to a product P – Eq. (*2*).

$$A \xrightarrow{h\nu} C \qquad (1)$$

$$S \xrightarrow{C} P \qquad (2)$$

In photocatalytic dioxygen reactions[4,5], the first step is photoreduction of transition metal ions; their lower oxidation states are able to coordinate dioxygen, and in this way dioxygen is activated by a catalyst formed photochemically in situ. The electron for the precursor reduction is provided by the substrate itself or by an indifferent absorbing species (e.g. sensitizer).

The concept of photocatalytic mechanism described above is so far the only way to explain the so-called post-irradiation effects together with quantum yields significantly exceeding unity and induction periods in photoinitiated reactions.

In the present paper, photoinitiated oxidation of two-carbon organic compounds by dioxygen was studied with the aim to elucidate the mechanism of Fe(III) action. The two-carbon substrates represent the simplest organic components of natural waters[6] with typical reactive functional groups.

EXPERIMENTAL

Chemicals

Substrates as well as sensitizer were used as supplied without further purification: glycolic acid (Loba-Chemie), glyoxalic acid (Merck), thioglycolic acid (Laborchemie Apolda), glycolaldehyde (Loba-Chemie), glyoxal (Aldrich), ethylene glycol (Lachema), glycine (Lachema), and sodium anthraquinone-2-sulfonate (Merck). Fresh solutions of substrates and sensitizer in double-distilled water were prepared daily.

The stock solution of $FeCl_3$ in 0.1 M HCl as well as the stock solution of the sensitizer were kept in dark.

Apparatus and Procedures

Irradiation procedure: Substrate solution (0.005 – 0.5 mol l^{-1}, 20 ml) was vigorously shaken with oxygen in a thermostatted (25 °C) quartz vessel and irradiated with a Tesla RVK 400 medium pressure mercury lamp (400 W). The emission characteristics of the lamp[7] show intense lines at 303, 313, 365, 435, 564, and 577 nm. The amount of oxygen consumed for a substrate oxidation was measured volumetrically by a gas burette; the accuracy of volumetric measurement was ±0.22 ml O_2 (the whole apparatus was thoroughly isolated and thermostatted), and the reproducibility was better than 3%.

Carbon dioxide, when liberated, was absorbed at the top of the reaction vessel by 40% KOH. Kinetic profiles (O_2 consumption vs time) were followed for 90 min.

Determination of quantum yields: the radiation was monochromatized by a UV KSIF 313 metal interference filter (Zeiss, Jena); the filter transmits lines with wavelength of 297, 303 and 313 nm. The light flux incident upon the reaction vessel was determined by ferrioxalate actinometry[8]. Since the geometry in the radiation intensity measurement was the same as in measuring the rate of O_2 consumption, and since the light flux did not change significantly with time, it was assumed that the light flux incident upon the reaction cell in the photochemical reaction was the same as that in the actinometric experiment. In the reaction systems where the stoichiometry substrate–O_2 is known, the quantum yields refer to the substrate transformed (glyoxalic acid, glyoxal); in the remaining systems (thioglycolic acid, glycolaldehyde), the quantum yields refer to the amount of O_2 consumed in the respective reaction.

Concentration of Fe^{2+} ions was determined spectrophotometrically with 1,10-phenanthroline (λ_{max} 510 nm, ε_{510} 1.1 . 10^4 mol^{-1} l cm^{-1}). Absorption spectra was measured on a Beckman DB-G spectrophotometer. For simulation of kinetic curves the method described in refs[9 – 11] was addopted.

RESULTS AND DISCUSSION

For each substrate thermal (dark) as well as photoinitiated reaction with O_2 were investigated, both with and without the addition of ferric ions.

Thermal reaction was observed solely with thioglycolic acid upon addition of ferric ions as a catalyst (at a concentration greater than 3 . 10^{-5} mol l^{-1}).

Glycolaldehyde, glyoxal, glycolic acid and glyoxalic acids required an addition of catalyst (ferric ions) even for photochemical reaction. Ethylene glycol and glycine did not react with dioxygen to a measurable extent under the condition used. Examples of variation in O_2 consumption with time for photoinitiated reactions of the substrate are shown in Fig. 1.

Photochemical oxidation of the substrates is influenced significantly by metal ions. Since the substrates themselves do not absorb at all or absorb negligibly the initiating radiation, no reaction can be expected in a pure substrate solution. After the addition of ferric ions, new absorption bands appear in the photodynamic region (Fig. 2); these bands are apparently due to the formation of a metal–substrate complex. Since the reaction of the substrates generally depends on the concentration of Fe^{3+} ions in the catalytic range (10^{-4} to 10^{-3} mol l^{-1}) and a saturation effect occurs at higher Fe^{3+} concentrations (Fig. 3), the catalytic action of metal ions in metal–substrate complexes rather than direct reaction of excited complexes with dioxygen was assumed. The catalytic action of ferric ions was tested by searching for post-irradiation effect, i.e. whether the reaction continues after irradiation is terminated. A post-irradiation effect is considered to indicate that photochemical generation of a catalyst may be involved in the reaction mechanism[2,12]. In these experiments the reaction were carried out intermittently in the light (shutter open) and in the dark (shutter closed); the oxygen consumption was measured continuously throughout the light and the dark periods. The reaction systems investigated in the paper fall into three groups:

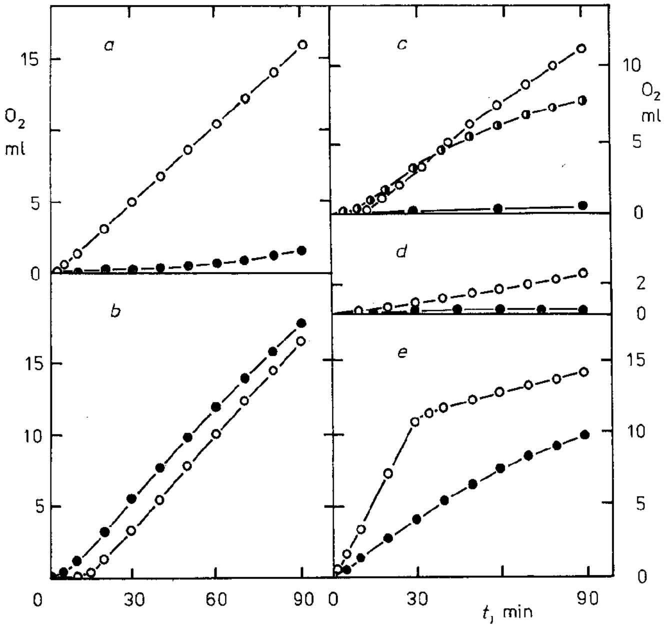

FIG. 1

Plots of O_2 consumption vs time for catalyzed and uncatalyzed photoreactions of substrates with dioxygen at 25 °C. *a* ● 0.1 M glyoxal, pH 3.5; ❍ 0.1 M glyoxal + 2 . 10^{-4} M $FeCl_3$, pH 3.4; *b* ● 0.1 M glycolaldehyde, pH 3.6; ❍ 0.1 M glycolaldehyde + 2 . 10^{-4} M $FeCl_3$, pH 3.6; *c* ● 0.1 M glyoxalic acid, pH 8.9; ❍ 0.1 M glyoxalic acid + 2 . 10^{-4} M $FeCl_3$, pH 9.0. ❍ 0.1 M glyoxalic acid + 1 . 10^{-4} M anthraquinone-2-sulfonate, pH 6.9; *d* ● 0.1 M glycolic acid, pH 8.7; ❍ 0.1 M glycolic acid + 2 . 10^{-4} M $FeCl_3$, pH 8.7; *e* ● 0.1 M thioglycolic acid, pH 8.3; ❍ 0.1 M thioglycolic acid + 1.6 10^{-5} M $FeCl_3$, pH 8.2

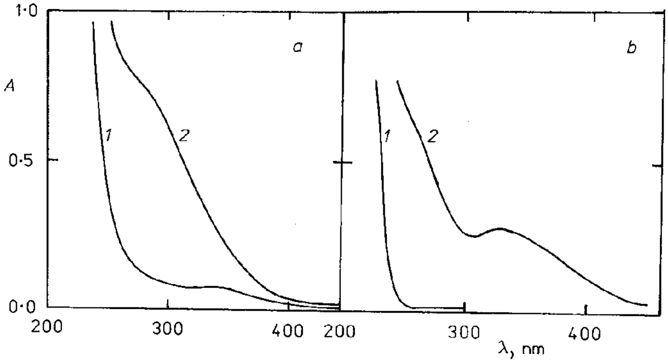

FIG. 2

Absorption spectra of *a* 0.1 M glyoxalic and *b* 0.1 M glycolic acids (curves *1*) and their complexes with Fe^{3+} ions (curves *2*). Concentration of Fe^{3+} ions is 2 . 10^{-4} mol l^{-1}, pH 8.5

1. Reaction systems with strong post-irradiation effects:
   - glyoxalic acid + Fe(III);
   - glyoxalic acid + anthraquinone-2-sulfonate (without Fe(III) added);
   - thioglycolic acid without Fe(III) added;
   - glyoxal + Fe(III).

Reaction (O_2 consumption) continues for more than 6 min with reaction rate comparable to that in the light periods.

2. Reaction system with a weak post-irradiation effect:
   - glycolaldehyde + Fe(III).

Reaction continues in the dark no longer than 2 – 3 min.

3. Reaction system with zero post-irradiation effect:
   - glycolaldehyde (no Fe(III) added).

Reaction stops immediately after the shutter is closed.

Examples of two reaction systems, one with a weak post-irradiation effect and the other with a strong post-irradiation effect, are shown in Fig. 4. In the case of strong post-irradiation effect, the effect is clearly more pronounced in every dark period as the overall irradiation time increases. In the systems with strong post-irradiation effects, the photocatalytic mechanism is assumed; in the system of thioglycolic acid where no catalyst was added, traces of metal ions might be responsible for the catalytic action. An evidence for the photocatalytic mechanism is the formation of the lower oxidation state of metal ions (ferrous ions). The Fe(II) concentrations were measured in the systems of glycine, glycolaldehyde, glyoxal, glycolic acid and glyoxalic acid, in O_2 satu-

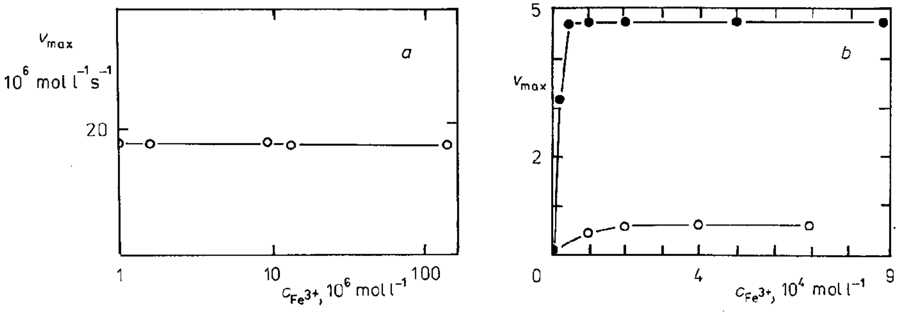

FIG. 3

Photoinitiated reaction of glycolic, glyoxalic acids and glycolaldehyde with O_2 – dependence of maximum reaction rates (v_{max}) on initial ferric ions concentration at the temperature 25.0 °C. *a* ❍ 0.075 M glycolaldehyde, pH 3.6; *b* ● 0.05 M glyoxalic acid, pH 9.0; ❍ 0.1 M glycolic acid, pH 9.2

rated solutions and under N_2. Under nitrogen, the rate of Fe(II) formation is identical with the rate of Fe(III) photoreduction. In O_2 saturated solution, the photochemically formed ferrous ions are reoxidized by O_2; relation between photoreduction and reoxidation rates depends on the nature of the substrate or generally, on the nature of the electron donor. As shown in Fig. 5, the behaviour of the substrates differs dramatically: with glycolaldehyde (*a*), glyoxalic acid (*b*) or glyoxal (*c*) as a substrate, the photoreduction of Fe(III) under N_2 is very fast and even in O_2 saturated solution the Fe^{2+} ions concentrations are rather high (25%, 94%, and 37%, respectively, of the total Fe added); with glycolic acid (*e*), a measurable concentration of Fe(II) was observed only under N_2, while in the system with glycine (*d*) the Fe(III) photoreduction does not proceed to a measurable extent even under N_2. The initial reaction rates of ferric ions photoreduction under N_2 are:

$3.8 \cdot 10^{-7}$ mol l^{-1} s^{-1} for glyoxalic acid,
$4.4 \cdot 10^{-7}$ mol l^{-1} s^{-1} for glycolaldehyde, and
$2.2 \cdot 10^{-8}$ mol l^{-1} s^{-1} for glycolic acid.

For glyoxalic acid there is a correlation between the ferrous ions concentration in the reaction system and O_2 consumption (Figs 5 and 2); the induction period in O_2 consumption is terminated when the concentration of Fe(II) formed in situ by photochemical reduction reaches $2 \cdot 10^{-5}$ mol l^{-1}. A similar effect on induction period was observed when Fe(II) as ferrous ammonium sulfate instead of Fe(III) was added into the reaction mixture.

The overall quantum yields, Φ_r, were measured in the system of glyoxalic acid, glycolaldehyde, glyoxal and thioglycolic acid. Their respective values are given in Table I.

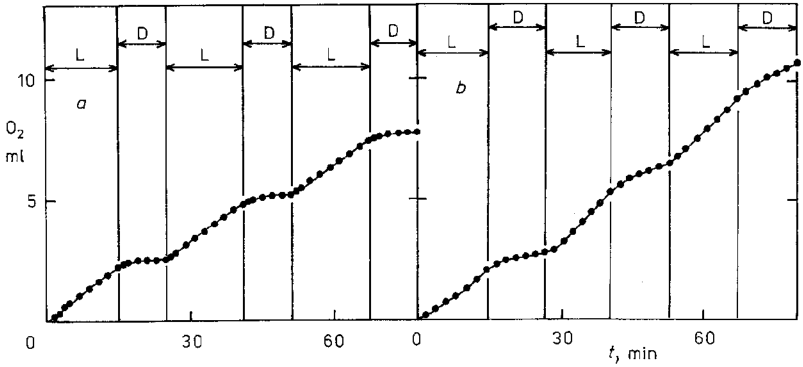

FIG. 4
Post-irradiation effects, plots of O_2 consumption vs time. Temperature 25 °C. *a* 0.075 M glycolaldehyde, pH 3.6; *b* 0.1 M glyoxal + $2 \cdot 10^{-4}$ M $FeCl_3$, pH 8.1. L irradiated (light) periods, D dark periods

The values of quantum yields are high, considering the relatively low reactivity of the substrates studied, nevertheless not exceeding unity by order, they do not form by themselves a strong proof for photocatalytic mechanism.

Photoinitiated reactions of two-carbon organic compounds were shown to be significantly affected by ferric ions. The post-irradiation effects observed in most systems can be explained excludingly by photocatalysis: photochemical formation of a catalyst catalyzing a thermal reaction of the substrate with dioxygen. The experimental data show a close correlation between the actual Fe(II) concentration in the reaction mixtures where Fe(III) was added and the overall reaction rates (oxygen uptake). The substrates studied contain nucleophilic (donor) groups and may therefore enter the coordination sphere of both Fe (III) and Fe(II). Photochemical formation of catalyst, i.e. photoreduction of ferric ions to ferrous ions, as well as deactivation of catalyst, i.e. reoxidation of ferrous ions by O_2, both depend on ligand nature (in the systems studied the only ligands present in the reaction mixture were the substrate and water molecules). In the systems, where the coordinated substrate enables fast reduction, ferrous ions are formed to the great extent even under O_2, and consequently, the oxidation of the substrates proceeds readily: glyoxalic acid + Fe(III), glycolaldehyde + Fe(III), glyoxal + Fe(III). On the

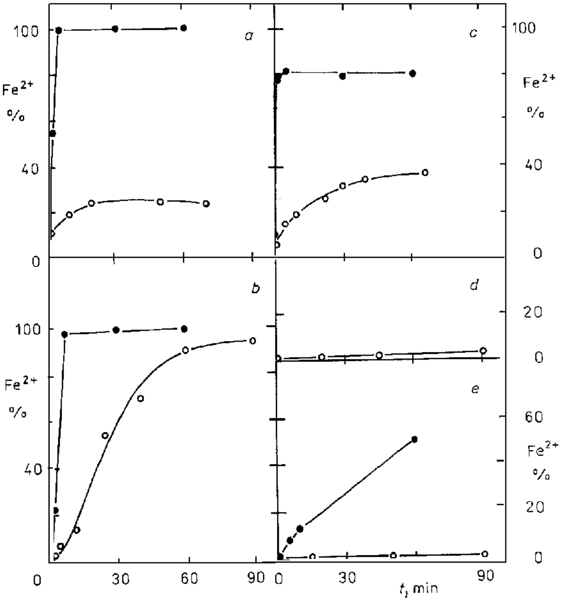

FIG. 5
Photoreduction of Fe(III) in O_2 saturated solutions (○) and under N_2 (●); concentration of $FeCl_3$ in all reactions was 2 . 10^{-4} mol l^{-1}. *a* 0.075 M glycolaldehyde; *b* 0.05 M glyoxalic acid; *c* 0.1 M glyoxal; *d* 0.1 M glycine; *e* 0.1 M glycolic acid

other hand, in several systems no ferrous ions were detected in O_2 saturated solutions and only a limited amount under N_2; in these systems reoxidation is as fast as photoreduction, hence little catalyst is present in the reaction mixture and the reaction with dioxygen is slow if measurable at all: glycolic acid + Fe(III), glycine + Fe(III). In two systems (thioglycolic acid, glyoxalic acid + anthraquinone-2-sulfonate), fast oxidation of the substrate (Fig. 1*c*, 1*e*) and considerable post-irradiation effects were observed, though no ferric ions were added to the reaction mixtures. It can be assumed that traces of metal ions present as impurities cause the catalytic effect[13], provided that the photoreduction of metal ions is fast enough.

The experimental findings presented in the paper are in agreement with the mechanism of cyclic generation of catalyst proposed by Veprek-Siska and coworkers[9 – 11]; the proposed mechanism involves three main steps:

– catalyst generation

$$\mathrm{M_{ox}} + \mathrm{S\ (substrate)} \xrightarrow[k_1]{h\nu\ \text{(or heat)}} \mathrm{M} + \mathrm{S_{ox}} \tag{3}$$

– catalyzed reaction

$$\mathrm{S} + \mathrm{O_2} \xrightarrow[k_2]{\mathrm{M}} \mathrm{P\ (product)} \tag{4}$$

– catalyst deactivation

$$\mathrm{M} + \mathrm{O_2} + \mathrm{H^+} \xrightarrow[k_3]{} \mathrm{M_{ox}} + \mathrm{H_2O\ (H_2O_2)}\ , \tag{5}$$

TABLE I
Overall quantum yields of reaction, Φ_r

Substrate	Reaction conditions	$\Phi_r{}^a$
Glyoxalic acid	1.6 . 10^{-4} M Fe(III)	0.664
Glyoxalic acid	without any Fe(III) added, reaction sensitized by 1.0 . 10^{-4} M anthraquinone-2-sulfonate	0.308
Glycolaldehyde	without Fe(III)	0.660
Glycolaldehyde	2.0. 10^{-4} M Fe(III)	0.402
Glyoxal	2.0. 10^{-4} M Fe(III)	1.174
Thioglycolic acid	without Fe(III)	1.050

[a] At 313 nm.

where M_{ox} is a metal ion (catalyst precursor), M is the reduced form of the metal ion (the catalyst), S_{ox} is the oxidized form of the substrate (a radical which is not supposed to propagate). Equation (*3*) represents thermal or photochemical reduction of Fe(III), Eq. (*4*) the Fe(II) catalyzed oxidation of the substrate, Eq. (*5*) the reoxidation of Fe(II), i.e. deactivation of catalyst.

Thermal reduction of Fe(III) occurs only in the case of thioglycolic acid[14,15]. In the systems with other substrates only photochemical reduction of Fe(III) was observed. The variation in the concentration of substrate and catalyst with time are given by differential Eqs (*6*) and (*7*), respectively, which are derived from Eqs (*3*) – (*5*).

$$-\frac{\mathrm{d[S]}}{\mathrm{d}t} = k_1\,[\mathrm{M_{ox}}]\,[\mathrm{S}] + k_2\,[\mathrm{M}]\,[\mathrm{S}]\,[\mathrm{O_2}] + I_\mathrm{a}\,\Phi \qquad (6)$$

$$\frac{\mathrm{d[M]}}{\mathrm{d}t} = k_1\,[\mathrm{M_{ox}}]\,[\mathrm{S}] - k_3\,[\mathrm{M}]\,[\mathrm{O_2}] + I_\mathrm{a}\,\Phi\,, \qquad (7)$$

where k_1 is the rate constant of thermal reduction of the metal ion M_{ox} by the substrate S, k_2 is the rate constant of the catalyzed reaction, k_3 is the rate constant of the oxidative catalyzed deactivation, I_a is the light intensity (in Einstein units) absorbed by catalyst precursor M_{ox} in unit time, Φ is the quantum yield of the photochemical generation of catalyst. For a solely photochemical reaction the first term in both Eqs (*6*) and (*7*) equals zero. The reaction rate d[S]/d*t* is proportional to the experimental overall reaction rate, *v*, measured as an oxygen consumption, the proportionality factor being the stoichiometry substrate : O_2.

Based on Eqs (*6*) and (*7*), the kinetic curves of O_2 consumption vs time for the system glyoxalic acid + Fe(III) were simulated using the method described by Lunak et al.[10]. The following known or experimentally determined data were used for the computation[7]: light intensity aquired from actinometric measurement, overall quantum yield of the reaction, Φ_r, concentration of O_2 in a solution saturated by O_2 at a given temperature, initial substrate and ferric ions concentrations, molar absorption coefficient of metal–substrate complex at 290 nm and the optical length of the reaction vessel. A series of curves with varied k_2 and k_3 were simulated and compared with experimental curve; one typical series of modelled curves together with the experimental curve is presented in Fig. 6. The value of k_2 for a pseudo-first-order reaction (steady-state concentration of the catalyst and the O_2 concentration at the given temperature) for the best-fitting simulated curve is $5.1 \,.\, 10^{-4}\ \mathrm{s}^{-1}$, which is in good agreement with the experimentally determined value of $k_{exp} = 4.4 \,.\, 10^{-4}\ \mathrm{s}^{-1}$ (see ref.[7]).

From the results presented in this paper it can be concluded that the photocatalytic effect of ferric ions is a common principle in the reaction mechanism of the two-carbon substrates oxidation by dioxygen. Entering the coordination sphere of metal (ferric) ions, the organic compounds form complexes which are the absorbing species in the reaction systems; Fe(III) complexes are photochemically reduced to Fe(II) complexes which are the active catalytic species in respective reaction systems. The overall reaction rate of substrate oxidation depends on the relation between the rate of Fe(III) photoreduction and the rate of Fe(II) reoxidation for the given substrate–metal complex, that is on the actual amount of the active catalytic species, Fe(II)–substrate complex.

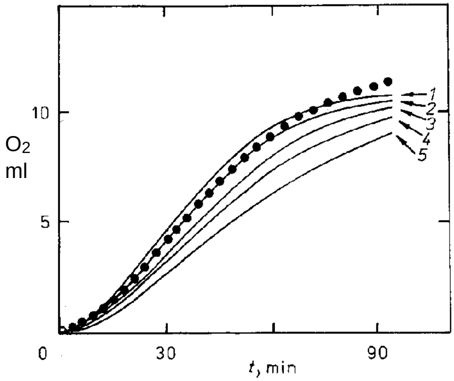

FIG. 6

Photoreduction of glyoxalic acid with Fe(III): model curves (*1* – *5*) for various constants k_2 and experimental curve (●) of O_2 consumption vs time. The model input values: light intensity, 2.16 . 10^{-7} mol quanta s^{-1}; overall quantum yield of the reaction, Φ_r, 0.664; steady state O_2 concentration, 0.001 mol l^{-1}; initial substrate concentration, 0.05 mol l^{-1}; initial ferric ions concentration, 1.6 . 10^{-4} mol l^{-1}; molar absorption coefficient of metal–substrate complex at 290 nm, 1 870 mol l^{-1} cm^{-1}; optical length of the reaction vessel 2 cm. Values of k_2 for individual model curves *1* 1.5 . 10^3 mol l^{-1} s^{-1}; *2* 1.9 . 10^3 mol l^{-1} s^{-1}; *3* 2.3 . 10^3 mol l^{-1} s^{-1}; *4* 2.7 . 10^3 mol l^{-1} s^{-1}; *5* 3.1 . 10^3 mol l^{-1} s^{-1}; (k_3 = 0)

REFERENCES

1. Miles C. J., Brezonik P. L.: Environ. Sci. Technol. *15*, 1089 (1981).
2. Hennig H., Rehorek D., Archer R. D.: Coord. Chem. Rev. *61*, 1 (1985).
3. Kutal C.: Coord. Chem. Rev. *64*, 191 (1985).
4. Veprek-Siska J., Lunak S., El-Wakil A.: Z. Naturforsch., B *29*, 812 (1974).
5. Veprek-Siska J., Lunak S.: J. Photochem. *8*, 391 (1978).
6. Gagosian R. B., Lee C. in: *Marine Organic Chemistry* (E. K. Duursma and R. Dawson, Eds), Elsevier Oceanographic Series 31, p. 91. Elsevier, New York 1981.

7. Klementova S., Wagnerova D. M.: Mar. Chem. *30*, 89 (1990).
8. S. L. Murov: *Handbook of Photochemistry*, p. 119. Dekker, New York 1973.
9. Veprek-Siska J., Lunak S., Mach I., Wagnerova D. M.: Oxidation Commun. *8*, 3 (1985/86).
10. Lunak S., Mach I., Wagnerova D. M., Veprek-Siska J.: Oxidation Commun. *8*, 19 (1985/86).
11. Wagnerova D. M., Mach I., Lunak S., Veprek-Siska J.: Collect. Czech. Chem. Commun. *54*, 3124 (1989).
12. Strohmeier W.: Chemie-Technik *4*, 433 (1975).
13. Veprek-Siska J.: Oxidation Commun. *8*, 301 (1985/86).
14. Schubert M.: J. Am. Chem. Soc. *54*, 4077 (1932).
15. Leussing D. L., Kolthof I. M.: J. Am. Chem. Soc. *75*, 3904 (1953).

Translated by the author (S. K.).