

Contribution to the Study of Quantum Efficiency of Photocatalytic Reaction of 2,6-Dichloroindophenol

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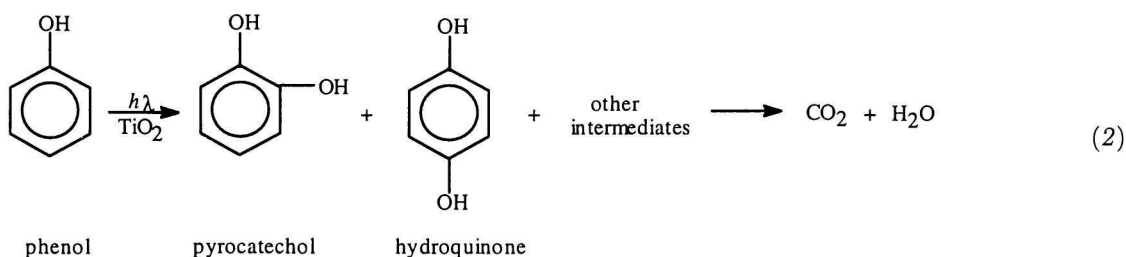
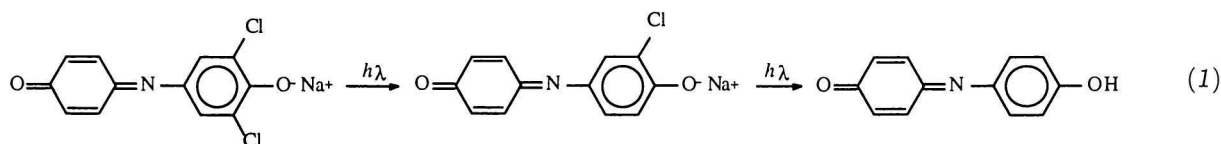
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Dedicated to Professor Vojtech Kellö, in honour of his 80th birthday

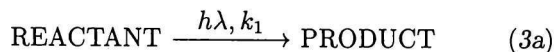
There is discussed a possibility of an apparent quantum yield definition for a simple type of photocatalytic reaction. This supposition is tested on a disproportionation of model compound – 2,6-dichloroindophenol through a comparison with phenol as a standard.

In her previous paper *Brezová* [1] suggested a simple way of determination of an integral efficiency of photocatalytic process in the given experimental arrangement by kinetic parameter of 2,6-dichloroindophenol (DCIP) disproportionation. We have tried to apply this idea on the phenol destruc-

tion through changes by HPLC measurement. At the same time for a comparison the destruction of 2,6-dichloroindophenol was studied. On the basis of literature data [2–4] it could be supposed that the mechanism of these processes may be described by the following integral equations



All of these processes are a little bit complicated as well. It means that for a simple case it enables to introduce an apparent kinetic constant of the first-order reaction

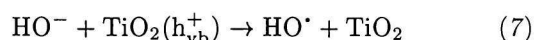
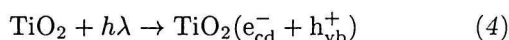


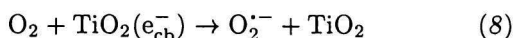
and then

$$-\frac{dc_{\text{DCIP}}}{dt} = kc_{\text{DCIP}} \quad (3b)$$

Derivation of a simplified equation is given in Appendix. With respect to a detailed mechanism we suppose a scheme described by *Sun and Bolton* [5]. According to this the high oxidative potential of the holes in the catalyst permits the direct oxidation of

organic matter (OM) to give reactive intermediates. In the case of TiO_2 it is commonly accepted that h_{vb}^+ is transformed into hydroxyl radicals from water molecule (HO^\bullet , eqn (6)). At the same time, the conduction band electrons reduce oxygen adsorbed on the surface of particle to form anion radicals $\text{O}_2^{\bullet-}$ [6]





The driving force of the heterogeneous electron transfer is the energy difference between the conduction band of TiO_2 and the reduction potential of the acceptor redox couple $A/A^{\cdot-}$

$$\Delta E = E_{\text{cb}} - E_{A/A^{\cdot-}} \quad (9)$$

Similarly, the holes in the TiO_2 valence band are open for the electron donation from the suitable electron donor [6].

The formed radicals are very reactive and can attack molecules of substrate. The radicals HO^{\cdot} do not migrate a long way from active centre on the surface of TiO_2 and therefore the reaction of these radicals with a molecule of organic substrate proceeds either on TiO_2 surface or in the distance of a few atoms from the surface [3].

The most of photodegradative reactions of organic pollutant use a chemical potential of holes. Of course a reducible substance must be present. This is valid in water medium. The redox processes then occur on the surface of semiconductor. For a given photocatalyst, total volume of layer of charge separation (*e.g.* zone of electron and hole separation) increases with decreasing TiO_2 particles diameter. For this reason there is advantage to utilize particles of colloid scale dimension. Reduction of particle size and degree coverage of one by transient metal are two ways of photocatalytic efficiency increase for the aqueous solution. The decrease of photocatalyst size is connected with a problem of its separation after the process.

There is used in literature as a quantum yield [7] the ratio of number of transformed molecules to the total number of photons incident to the reactor inside. As an integral apparent quantum yield Φ can be taken number N_{mol} of the reactant molecules undergoing a change to the number N_{ph} of quanta absorbed in the system [7]

$$\begin{aligned} \Phi_{\text{overall}} &= \frac{N_{\text{mol}}/(\text{cm}^{-3} \text{ s})}{N_{\text{ph}}/(\text{cm}^{-3} \text{ s})} = \\ &= \frac{\text{rate of reaction}}{\text{rate of absorption of radiation}} \end{aligned} \quad (10)$$

It is difficult to determine the N_{ph} with a good accuracy. For this reason Φ could be defined on the basis of a standard molecule disproportionation [7]

$$\Phi = \xi_r \Phi_{\text{stand}} \quad (11)$$

where ξ_r is a relative photonic efficiency. Under the same experimental conditions and supposing the same mechanism for disproportionation of the standard and the studied substrate for ξ_r it could be written

$$\xi_r = \frac{\text{rate of disappearance of substrate}}{\text{rate of disappearance of phenol}} \quad (12)$$

Table 1. The Values of Rate Constants and Relative Photonic Efficiencies for the Studied Compounds

Compound	$c(\text{TiO}_2)$ g dm ⁻³	k		ξ_r	
		min ⁻¹			
Phenol	0.5	0.00607			
	1.0	0.00755			
	1.5	0.00539			
	2.0	0.0043			
DCIP	0.5	0.03703 ^a	0.12697 ^b	1.33 ^a	5.44 ^b
	1.0	0.07451 ^a	0.17124 ^b	3.04 ^a	6.61 ^b
	1.5	0.05836 ^a	0.13221 ^b	2.73 ^a	5.74 ^b
	2.0	0.04285 ^a	0.12586 ^b	2.01 ^a	4.83 ^b

a) For $\lambda = 270$ nm; b) for $\lambda = 600$ nm.

This idea is applied in this study (Table 1). As a final equation for the first-order slowest reaction can be written the integral form

$$\ln \frac{a}{a-x} = k_1 t \quad (13)$$

where a is the starting value of DCIP concentration and $(a-x)$ is the same at time t .

EXPERIMENTAL

DCIP (Fluka) and phenol (Lachema) were of anal. grade used without any further purification. Photocatalyst was titanium dioxide TiO_2 Degussa P 25 (B.E.T. surface area $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$, predominantly anatase). Water was deionized.

Photodegradation was studied in the experimental set up described before [2]. The reaction suspension was bubbled by air at a constant temperature 30°C and a light source was medium-pressure Hg lamp in the pyrex sleeve 125 W (predominantly wavelength at 365 nm, significant amounts in the VIS region at 404, 418, 520, 575–580 nm). During the photodegradation, a sample of suspension was taken at various time intervals. Changes of pH and electric conductivity (Figs. 3, 4) were measured during reactions by a simple measuring device. Before other analysis the samples were centrifuged. The UV VIS spectra were measured by HITACHI U 3300. For the determination of the DCIP concentration changes, the absorption bands maxima at $\lambda = 270$ nm and $\lambda = 600$ nm were monitored (Fig. 2). Concentration changes of phenol were observed at $\lambda = 269$ nm (Fig. 1). Also the changes of phenol concentration in the samples were obtained using HPLC SHIMADZU LC 10A; column BIOSPHER SIC 18, 150×4.6 mm; column temperature: ambient; flow rate: $0.5 \text{ cm}^3 \text{ min}^{-1}$; mobile phase, acetonitrile H_2O in the ratio 40/60; detector SPD-M10 Avp, $\lambda = 269$ nm.

RESULTS AND DISCUSSION

In the laboratories, phenol is often used as a model

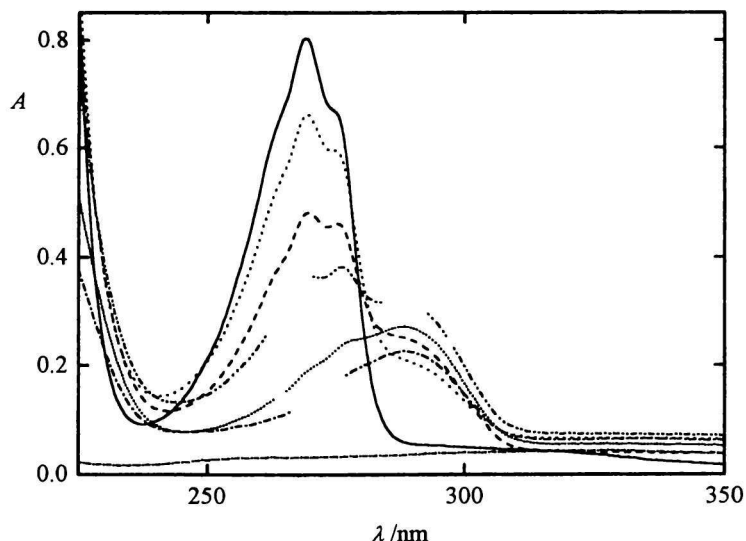


Fig. 1. The UV spectra of phenol solutions during photocatalytic degradation on TiO_2 (Degussa P 25) in the presence of air; $c_{\text{phenol}}^0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{TiO}_2} = 1.0 \text{ g dm}^{-3}$, cuvette width $\approx 1.0 \text{ cm}$. — 0 min; 30 min; --- 90 min; - · - · - 150 min; - - - 210 min; - · - · - 240 min; - - - 300 min.

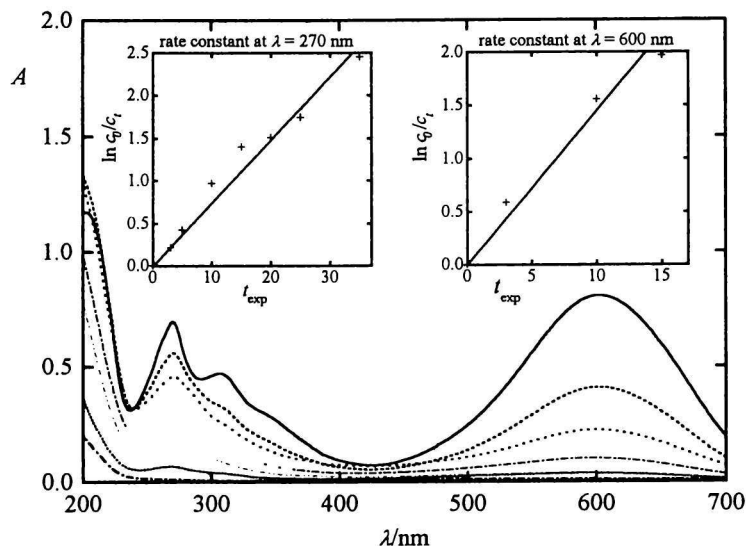


Fig. 2. The UV VIS spectra of DCIP solutions during photocatalytic degradation on TiO_2 (Degussa P 25) in the presence of air; $c_{\text{DCIP}}^0 = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{TiO}_2} = 1.0 \text{ g dm}^{-3}$, cuvette width $\approx 1.0 \text{ cm}$. — 0 min; 3 min; --- 5 min; - · - · - 10 min; - - - 15 min; - · - · - 35 min; - - - 55 min.

compound in set up reactors, for the calculation of efficiencies of decomposition and for searching the photocatalyst activity.

The crucial point is generation of hydroxyl radicals HO^\bullet of the photocatalytic process in aqueous solution. Two intermediates were detected by HPLC, catechol and quinone (eqn (2)). The retention times of these compounds were 2.1 min (quinone), 2.9 min (catechol), and 3.5 min (phenol). Identification was confirmed from chromatograms of pure compounds. Similar results were reached earlier [7].

The first reaction seems to be a determining step and for this reason kinetic description may be simplified in the following form

fied in the following form

$$c_{\text{phenol}} = c_{\text{phenol}}^0 e^{-kt} \quad (14)$$

where the individual symbols have their usual meaning. Experimental results of the study are comprised in Fig. 1.

The exact determination of phenol could not be connected with any problems. It was directly determined by the HPLC method under conditions mentioned a few lines above.

Photocatalytic oxidative degradation of DCIP on titanium dioxide in aqueous suspension caused by

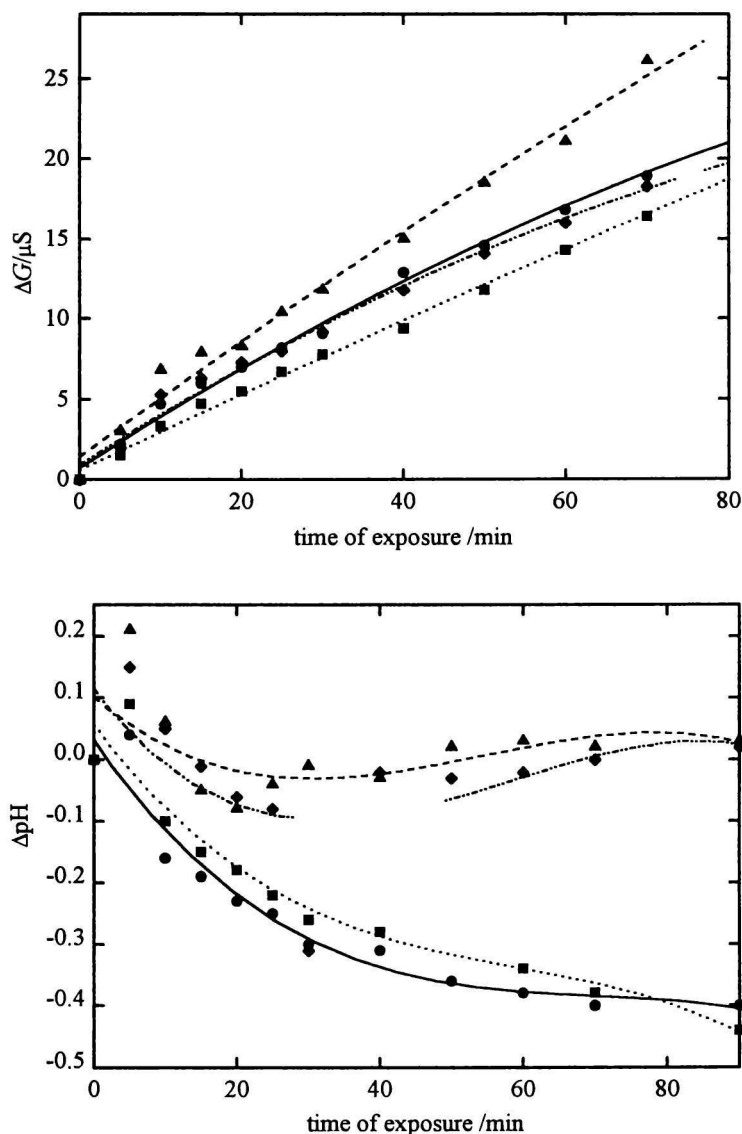
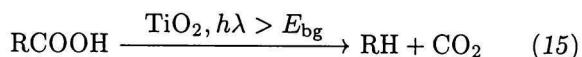


Fig. 3. Changes of electric conductivity and pH during photocatalytic degradation of phenol for different concentrations of TiO_2 (■ 0.5 g dm⁻³; ● 1.0 g dm⁻³; ▲ 1.5 g dm⁻³; ◆ 2.0 g dm⁻³ TiO_2).

medium-pressure Hg lamp is given in Fig. 2. Strongly oxidizing hydroxyl radicals (HO^\bullet) are produced during exposition. The oxidative attack of DCIP molecules adsorbed on the photocatalyst particles may be principally described by scheme (1).

The dechlorination seems to be the first step with successive oxidation leading to carboxyl group production. The last one is decomposed *via* the Kolbe photoreaction



CONCLUSION

There was found that for a simple characterization of an efficiency of a photocatalytic disproportionation

of organic phenolic compounds the ratio of rate of disappearance of studied compound and a standard one should be used as a measure of quantum efficiency. DCIP seems to be the most appropriate as studied compound, its application has a few advantages:

- its kinetic value of photocatalytic transformation allows to compare many of the other compounds of the same type,

- the content of chlorine bonded in the DCIP molecule gives us a possibility to characterize a wide range of organic chlorinated compounds.

The concentration of the photocatalyst at the highest rate constant was found to be optimal (1.0 g $TiO_2/1000\text{ cm}^3$ of solution). At the same time the highest relative photonic efficiencies were found for this concentration of the photocatalyst. The similar ξ_r values of phenolic derivatives were introduced by *Serpone et al.* [7]. During the light exposition changes

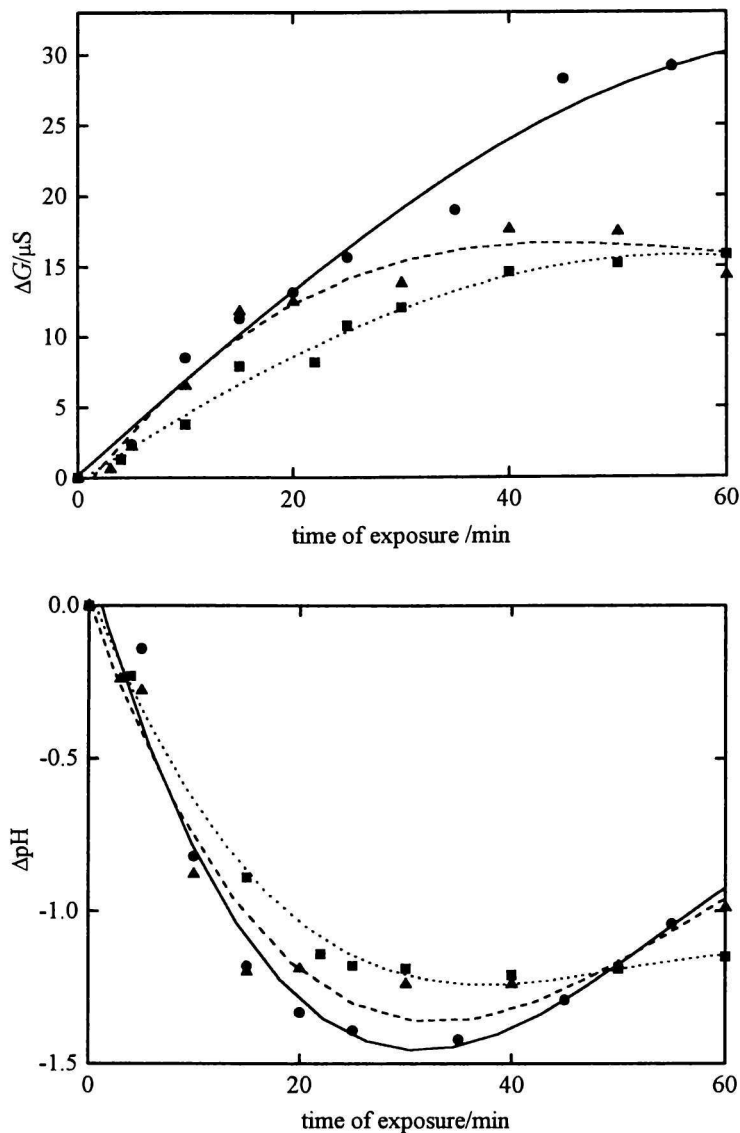


Fig. 4. Changes of electric conductivity and pH during photocatalytic degradation of 2,6-dichloroindophenol for different concentrations of TiO₂ (■ 0.5 g dm⁻³; ● 1.0 g dm⁻³; ▲ 1.5 g dm⁻³ TiO₂).

of acidity of the aqueous solutions of the studied compound have been observed, as well as the changes of electric conductivity.

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APPENDIX

At the first approach we can suppose that the concentration of DCIP is small enough, so it could be written

$$-\frac{dc_{\text{DCIP}}}{dt} = kc_{\text{DCIP}} \quad (A.1) \equiv (3b)$$

As the DCIP concentration is measured through

the Lambert—Beer law as well, it could be written

$$I = I_0(1 - e^{-\alpha cl}) \quad (\text{A.2})$$

$$\frac{I_0}{\Delta I} = e^{\alpha cl} \quad (\text{A.3})$$

$$\ln \frac{I_0}{\Delta I} = \alpha cl \quad (\text{A.4})$$

$$A = \alpha cl \quad c = \frac{A}{\alpha l} \quad (\text{A.5})$$

$$-\frac{d\left(\frac{A}{\alpha l}\right)}{dt} = k \frac{A}{\alpha l} \quad (\text{A.6})$$

$$\frac{dA}{A} = -k dt \quad (\text{A.7})$$

$$\ln \frac{A}{A_0} = -kt \quad (\text{A.8})$$