Photocatalytic oxidation of 2,6-dichloroindophenol in the titanium dioxide aqueous suspension

V. BREZOVÁ, M. ČEPPAN, M. VESELÝ, and L. LAPČÍK

Department of Textile, Pulp, and Paper, Faculty of Chemical Technology, Slovak Technical University, CS-812 37 Bratislava

Received 12 January 1990

Dedicated to Professor L. Valko, DrSc., in honour of his 60th birthday

Photocatalytic oxidation of sodium salt of 2,6-dichloroindophenol (DCIP) in titanium dioxide aqueous suspension has been studied. DCIP is photocatalytically oxidized on the active TiO_2 surface by the medium pressure Hg lamp with pyrex sleeve radiation ($\lambda > 280$ nm). The apparent integral quantum yield of the DCIP decomposition was determined. Photocatalytic decomposition of DCIP in aqueous suspension of TiO_2 can be described by the formal first-order kinetics. The same results can be obtained for TiO_2 (P25) during the Hg lamp irradiation and solar exposure as well. The reaction is suitable for testing of the semiconductor powder photocatalytic activity.

Photochemical reactions on semiconductor powders, called photocatalytic reactions, attract the great attention of photochemists and electrochemists. The research is concentrated first of all on the four topics: *a*) water cleavage into oxygen and hydrogen [1—3], *b*) obtaining of energy-rich gases from renewable or waste materials [4—6], *c*) nonconventional methods in organic synthesis [7—10], *d*) purification of waste water from organic or inorganic compounds [11—18].

Band theory of solids and electronic theory of catalysis have been successfully utilized for understanding and rationalization of various photoprocesses studied on the semiconductor electrodes and semiconductor powder systems. According to the band model, the existence and efficiency of different photoredox processes are related with valence band position (the highest occupied energy band) and conductance band position (the lowest unoccupied energy band). Semiconductor band gap energy E_{bg} is characterized by the difference between the edges of conductance and valence bands [19]. Absorption of the light with energy $E > E_{bg}$ leads to creation of electron (e^-) and hole (h^+) pairs which move in the conductance or valence band owing to an electric field. Resulting equi-

librium distribution of electrons and holes causes reduction or oxidation processes with adsorbed species or with surface groups [20].

Quantum yield q is the basic characteristic of the photochemical reaction. An experimental system for measurement of photochemical reaction quantum yields has to enable to determine source radiant flux in the reaction mixture. This can be managed by changing the reaction solution for an actinometric system in an optical set [20]. The situation is more complicated in the case of photocatalytic reactions. The quantum yield in a photocatalytic suspension cannot be measured exactly due to the disturbing light scattering effect and the reflection by the photocatalyst grains [21].

According to *Pichat et al.*, the number of photons, absorbable by the photocatalyst per radiant flux unit, can be calculated from the lamp spectral distribution, spectral transmission of the used optical glasses and filters, and photocatalyst reflectance spectrum.

The photocatalytic reaction quantum yield can be expressed as follows [21]

$$q_A = \frac{n_A}{n_f P_0 \delta (1 - R)} \qquad (1)$$

where n_A, n_f is the number of the product molecules and of photons, absorbable by the photocatalyst per radiant flux unit, respectively, P_0 is the incident radiant flux, R is the photocatalyst reflectivity, $\delta = (P_0 - P_t)/P_0$ is the correction coefficient which must be introduced into eqn (*1*) if the amount of the photocatalyst is not sufficient to absorb completely the incident light flux; P_t is the nonabsorbed radiant flux passing through the reaction system.

Titanium dioxide which is often used as active semiconductor has relatively large band gap energy (3.02—3.2 eV); it is stable in aqueous solutions and, moreover, it is photocorrosion-proof [22]. TiO_2 photocatalytic activity is modified by its crystal structure (rutile, anatase) [23], thermal pretreatment method [24], surface area [25] and additives [26]. Photochemical activity of titanium dioxide of various origin is very different, therefore it is useful to test the TiO_2 sample before the photocatalytic reaction by means of suitable testing reaction (*e.g.* decarboxylation of acetic acid [27], oxidation of 2-propanol [24]).

The aim of this paper is to propose the application of the photocatalytical reaction of 2,6-dichloroindophenol on the TiO_2 surface as the testing process for the photocatalysts activity.

Experimental

The photocatalytic oxidation of sodium salt of 2,6-dichloroindophenol (DCIP) in titanium dioxide aqueous suspension has been studied. DCIP solutions with concentrations of 0.33×10^{-3} mol dm^{-3} were used for experimental measurements. DCIP solutions with concentration of 0.44×10^{-3} mol dm^{-3} were used for continual estimation of carbon dioxide. The prepared aqueous suspension of DCIP and TiO_2 was stirred for 20 min in an ultrasonic apparatus (Tesla, Vráble, CSFR), poured out into the photochemical well, tempered to temperature of 30 °C and taken as the zero sample. The following TiO_2 samples were applied:

a) TiO_2 (P25; Degussa, FRG), predominantly anatase [28], B.E.T. surface area 50 ∓ 15 m^2 g^{-1},

b) TiO_2 (anatase; Chemical Works, Přerov, CSFR), surface area unknown,

c) TiO_2 (rutile; Chemical Works, Přerov), surface area unknown,

d) Pt (2 mass %)/TiO_2 (P25); platinum was deposited on TiO_2 surface photocatalytically from aqueous Na_2PtCl_6 solution in the presence of methanol [29, 30].

All chemicals used were of anal. grade purity (Lachema, Brno). Uranyl oxalate was a laboratory preparation obtained according to [31]. Aqueous solutions were prepared in distilled water obtained by water distillation, after pretreatment on Wofatit KPS 200 cation exchanger (Kavalier, CSFR).

Photocatalytic experiments were carried out in photochemical immersion well (Applied Photophysics, London). Pyrex sleeve with 125 W medium pressure Hg lamp was inserted to quartz cell with distilled water in the cooling thimble (30 °C). Medium pressure lamps emit predominantly radiation at $\lambda = 365$—366 nm with small amounts in the ultraviolet region at $\lambda = 265$, 297, 303, 313, and 334 nm and significant amounts in the visible region at $\lambda = 404$—408, 436, 546, and 577—579 nm. The reaction suspension was bubbled by cleaned air (by flow rate 530 cm^3 min^{-1}) through the sintered glass located at the bottom of the well. The samples from the well were centrifuged for 25 min at 6400 *g* on the Janetzki T24 ultracentrifuge.

The carbon dioxide was estimated conductometrically *via* continual measurement of the conductivity of barium hydroxide solution in suitably arranged cell, into which the gas products of photocatalytic reaction were introduced through the sintered glass. A linear recorder, connected directly to the conductometer OK 102/1 (Radelkis, Budapest), registered the conductivity time changes. The concentration changes of DCIP solution were estimated spectrophotometrically by the UV VIS spectrophotometer PU 8800 (Philips). Calibration curves were obtained by the absorbance measurements of the DCIP solution with known concentration. Due to expressive decrease of the solution pH during the photocatalytic oxidation, it was not suitable to use the absorption band maximum at $\lambda = 600$ nm for the determination of DCIP concentration (Fig. 5, curve *A*). Location and intensity of this band is changed significantly with pH value. For the determination of the DCIP solutions concentrations, the absorption band maximum at $\lambda = 270$ nm was monitored. Reflectance UV/VIS spectra of the TiO_2 samples were measured by the UV VIS spectrophotometer M40 (Zeiss, Jena) with the reflectance

accessory equipment with the integration sphere. The pH values were measured by the digital pH-meter OP-211/1 (Radelkis, Budapest), a combined glass electrode was used. Thin-layer chromatography (TLC) of the reaction products was carried out on the Silufol plates (Kavalier, Votice, CSFR) in the benzene—ethyl acetate system ($\varphi_r = 4:1$); ammonia vapour was used for the spot visualization [32].

Results and discussion

Determination of photocatalytic reaction quantum yield

Experimental arrangement of the photochemical well with the pyrex Hg lamp sleeve eliminated the low limit region of the active radiation approximately to $\lambda = 280$ nm. The upper limit of the effective radiation is defined by the TiO_2 energy band gap (anatase 380 nm, rutile 410 nm). The suitable liquid filter, transmitting only in the efficient radiation region, was defined by demanding wavelengths interval. The liquid filter of the solution of $CoCl_2$ $6H_2O$ ($\varrho = 200\ g\,dm^{-3}$) and $NiCl_2 \cdot 6H_2O$ ($\varrho = 100\ g\,dm^{-3}$) in the aqueous mixture of 65 % ethanol and 1 M-HCl (35 %) was used for the wavelengths interval of 280—380 nm [31]. The aqueous solution of $CoSO_4 \cdot 7H_2O$ ($\varrho = 240\ g\,dm^{-3}$) was used as the filter for the wavelengths interval of 280—410 nm [33].

Actinometric experiments were realized under the same conditions as the photocatalytic DCIP oxidation. The radiant flux, absorbable by the titanium dioxide (*i.e.* in eqn (*1*) $n_f P_0$ product), was determined using the uranyl oxalate actinometer.

The photocatalytic reaction apparent quantum yield was calculated from the approximated values [34] of:

a) the average quantum yield of the uranyl oxalate actinometer, calculated as the arithmetic mean of the quantum yields at the wavelengths emitted by medium pressure Hg lamp [31],

b) the liquid filter average transmittance, which was calculated from the overlap area of the spectral curves of transmittances of liquid filter and pyrex sleeve (57 % for the 280—380 nm region, 46 % for the 280—410 nm region),

c) the titanium dioxide average reflectivity R_{av} which was determined by the reflectance UV/VIS spectra measurements of powder samples

$$[R_{P25}(280—380)]_{av} = 0.1$$
$$[R_{anatase}(280—380)]_{av} = 0.13$$
$$[R_{rutile}(280—410)]_{av} = 0.095$$

d) the correction factor of eqn (*1*) $\delta = 1$ because the experiment was arranged to reach the complex absorption of the incident flux in the reaction system.

Table 1

The dependence of the formal rate constant and of the DCIP degradation apparent integral quantum yield on the TiO_2 content in suspension

$w(TiO_2$ (P25))/%	$\frac{k}{min^{-1}}$	q_A
0.75	0.15 ∓ 0.03	0.0019
0.66	0.183 ∓ 0.006	0.0022
0.5	0.19 ∓ 0.02	0.0027
0.375	0.22 ∓ 0.02	0.0028
0.25	0.22 ∓ 0.03	0.0027
0.124	0.19 ∓ 0.007	0.0025
0.0625	0.18 ∓ 0.01	0.0025
0.0312	0.048 ∓ 0.008	0.0017
0.5 (rutile)	0	0
0.5 (anatase)	0.02 ∓ 0.002	0.0013
0	0.0023 ∓ 0.0004	—

The apparent integral quantum yield of the DCIP decomposition (Table 1) and the apparent integral quantum yield of the carbon dioxide formation was calculated using eqn (*1*).

Dark reaction

During the sonication of aqueous DCIP and TiO_2 suspension the DCIP solution concentration is decreased significantly. This can be explained by the DCIP adsorption on the TiO_2 powder surface [35]. Therefore the DCIP adsorption on the TiO_2 (P25) surface was followed during the sonication (Fig. 1). The DCIP concentration in the solution and on the TiO_2 surface c_{ads} during the stirring was determined spectrophotometrically after the centrifugation. However, the sonication is not isothermal, the sample has been warmed. The stabilization of the adsorption equilibrium in the solution can be assumed during the centrifugation, which caused the greater dispersion variance of the measured points (Fig. 1).

The solution concentration changes were not observed (Fig. 2, curve *2*) during the experiment, performed under the same conditions as the photocatalytic reaction but without the medium pressure 125 W Hg lamp radiation.

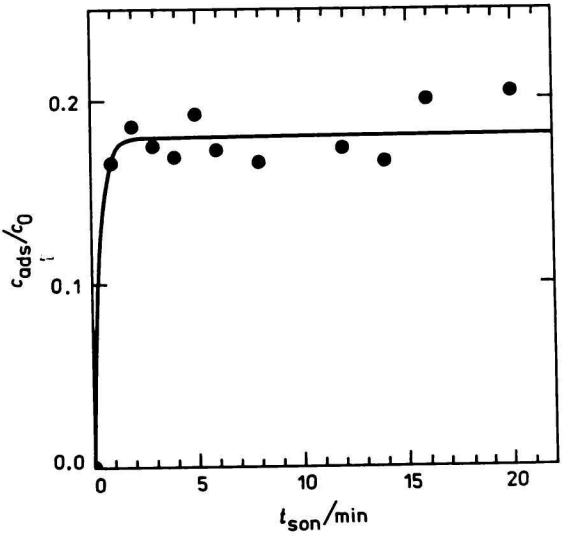


Fig. 1. The relative concentration changes of DCIP during the sonication of aqueous suspension of TiO_2 (P25). 0.5 g TiO_2/100 g DCIP solution.

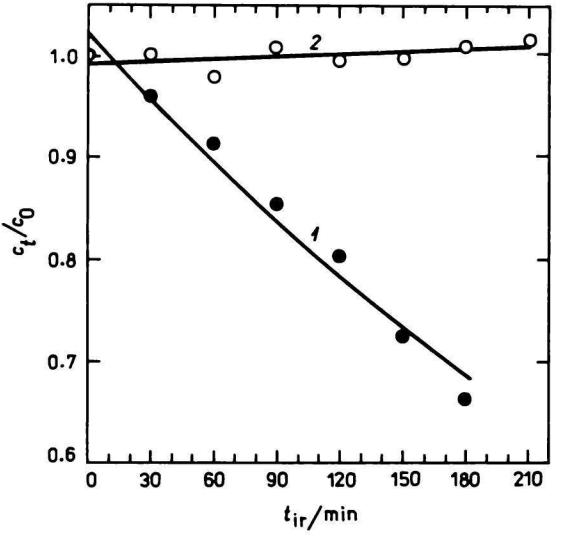


Fig. 2. The relative concentration changes of DCIP. *1.* Irradiation of DCIP aqueous solution without TiO_2; *2.* 0.5 g TiO_2/100 g DCIP solution without irradiation.

DCIP *photochemical decomposition*

The irradiation of the DCIP solution by the medium pressure 125 W Hg lamp in the above-mentioned system leads to the DCIP concentration changes (Fig. 2, curve *1*). The shift of the absorption band maximum of 270 nm to shorter wavelength (263 nm, Fig. 3) was observed in the UV spectra of irradiated solutions. In the TLC of the irradiated samples on the Silufol plates, three clear resolved spots were determined the intensities of which were time-dependent.

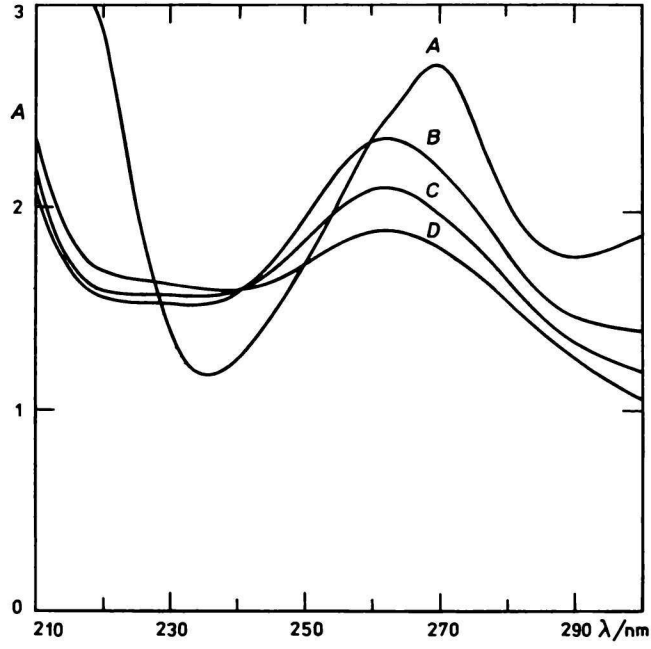
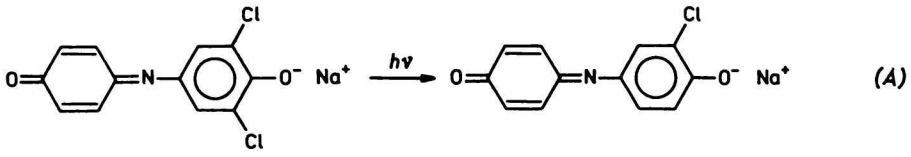


Fig. 3. The UV spectrum changes of DCIP aqueous solution during irradiation. Time: *A*. 0 min; *B*. 120 min; *C*. 150 min; *D*. 180 min.

The spot with the value of retention factor $R_f = 0.29$ corresponds to DCIP, the spot with $R_f = 0.19$ corresponds probably to monochloroindophenol (CIP), and the spot with $R_f = 0.13$ corresponding to indophenol (IP), was assigned by the standard. The stepwise photochemical DCIP dechlorination can be assumed (eqns (*A*, *B*)).

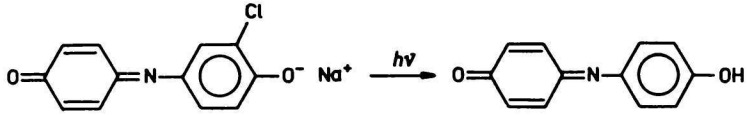
Photochemical DCIP dechlorination can be described by the formal first--order kinetic equation

$$\ln \frac{c_0}{c_t} = k\,t \qquad (2)$$



(A)

DCIP CIP



(B)

CIP IP

where c_0, c_t are the DCIP concentrations at the time $t = 0$ and at the time t, k is the rate constant. The rate constant values can be calculated by the linear regression method from eqn (*2*) (Table 1).

Photocatalytic decomposition of the DCIP *aqueous solution on* TiO_2

Irradiation of the DCIP aqueous solution in the presence of TiO_2 (P25) caused a rapid decomposition (Fig. 4, curves *1*—*3*). The suspension colour

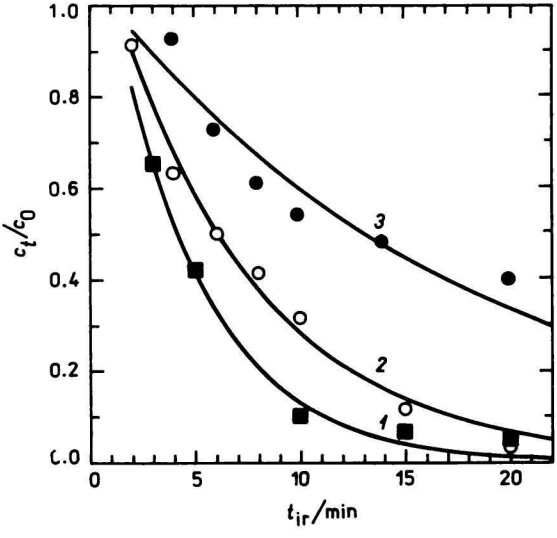


Fig. 4. The changes of the relative DCIP concentration during photocatalytical degradation on TiO_2 (P25). *1.* 0.75 g TiO_2/100 g DCIP solution; *2.* 0.06 g TiO_2/100 g DCIP solution; *3.* 0.03 g TiO_2/100 g DCIP solution.

change from blue to pink and to white can be observed during this decomposition (Fig. 5). The DCIP photocatalytic degradation in aqueous suspension of TiO_2 can be described after *ca.* 2 min by the formal first-order kinetics and the rate constant value can be calculated from eqn (*2*). The changes of the rate constant of the photocatalytic decomposition were followed up with the changing amount of TiO_2 (P25) in the photochemical well in the experimental arrangement (Table 1). It was found that small amount of TiO_2 is sufficient (0.05 g/100 g DCIP solution) for obtaining the high decomposition rate. The photocatalytic DCIP decomposition in the aqueous suspension of TiO_2 is accompanied by the significant pH decrease, which is in accordance with published oxidative mechanisms [35] of organic compounds on the TiO_2 surface (Fig. 6, curve *1*).

The reactive hydroxyl radical and hydrogen peroxide is formed in the aqueous suspension of TiO_2 during irradiation in the presence of oxygen [36]

$$TiO_2 \xrightarrow{h\nu > E_{bg}} h^+ + e^- \qquad (C)$$

$$(Ti{-}OH^-)_{surf} + h^+ \rightarrow (Ti{-}OH^{\bullet})_{surf} \qquad (D)$$

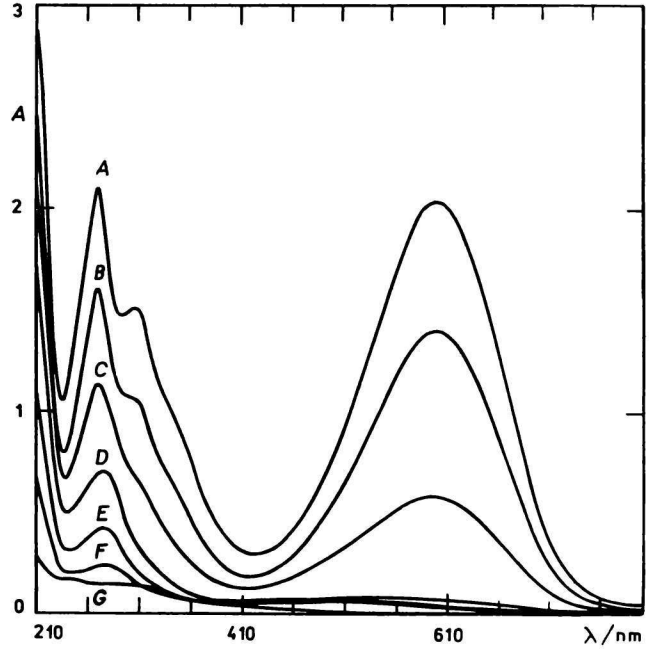


Fig. 5. The UV/VIS spectra changes of DCIP solution during photocatalytical degradation on TiO_2 (P25). 0.5 g TiO_2/100 g DCIP solution. Time: *A.* 0 min; *B.* 2 min; *C.* 4 min; *D.* 6 min; *E.* 8 min; *F.* 10 min; *G.* 15 min.

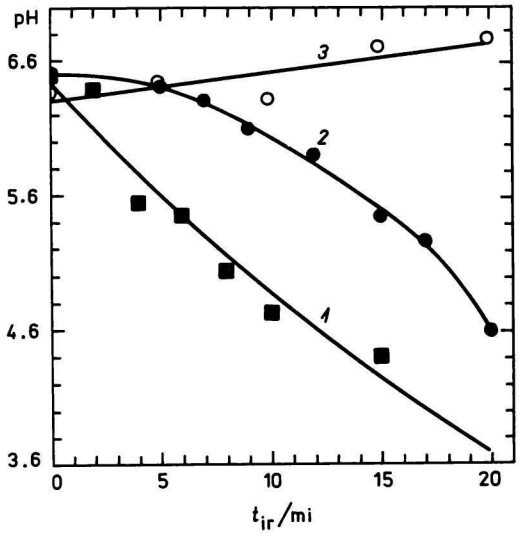


Fig. 6. The changes of the pH values of DCIP aqueous solution during photocatalytical degradation on TiO_2. *1.* 0.375 g TiO_2 (P25)/100 g DCIP solution; *2.* 0.5 g TiO_2 (anatase)/100 g DCIP solution; *3.* 0.5 g TiO_2 (rutile)/ /100 g DCIP solution.

$$(\text{Ti—OH}^{\bullet})_{\text{surf}} + (\text{OH}^{-} \quad \text{H}_2\text{O})_{\text{phys}} \rightarrow (\text{Ti—OH}^{-})_{\text{surf}} + \text{OH}^{\bullet}_{\text{phys}} \qquad (E)$$

$$\text{OH}^{\bullet}_{\text{phys}} + \text{OH}^{\bullet}_{\text{phys}} \rightarrow (\text{H}_2\text{O}_2)_{\text{phys}} \qquad (F)$$

$$(\text{Ti—H}_2\text{O})_{\text{surf}} + (\text{H}_2\text{O}_2)_{\text{phys}} \rightarrow (\text{Ti—H}_2\text{O}_2)_{\text{surf}} + \text{H}_2\text{O} \qquad (G)$$

The hydroxyl radical can attack the adsorbed DCIP molecule and can cause its quinoid and benzoid part oxidation.

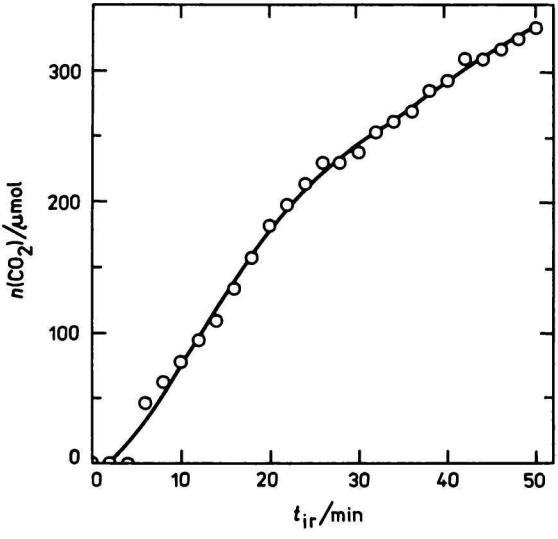


Fig. 7. The carbon dioxide formation during the photocatalytical degradation of DCIP solution on TiO_2 (P25). 0.43 g TiO_2/100 g DCIP solution, c(DCIP) = 0.44 mmol dm^{-3}, V(DCIP) = 70 cm^3.

By the TLC of the samples irradiated less than 8 min, in addition to DCIP spot ($R_f = 0.29$), the spot with $R_f = 0.19$ was observed on the plate as well. However, both spots with the prolonging of exposition time disappeared. The proposed mechanism is supported by this fact. The first stages of the photocatalytic reaction are probably the dechlorination, followed by the oxidation of the molecular carbon skeleton and carboxylic acids formation [15, 35].

Carboxylic acids decarboxylate on TiO_2 very easy by Kolbe photoreaction [27]

$$\text{R—COOH} \xrightarrow[h\nu > E_{bg}]{TiO_2} \text{RH} + CO_2 \qquad (H)$$

Carbon dioxide formation from DCIP in aqueous suspension of TiO_2 by photocatalytic degradation is confirmed by the continual conductivity estimation of the barium hydroxide solution. The calibration curve was obtained by the conductivity measurements of the $Ba(OH)_2$ solutions of known concentration. The amount of substance of formed CO_2 was calculated from the time dependence of the $Ba(OH)_2$ solution conductivity (Fig. 7). It was found that CO_2 amount of substance formed during 50 min irradiation of the DCIP in aqueous suspension of TiO_2 corresponds to 90 % DCIP mineralization to CO_2. The apparent integral quantum yield of the CO_2 formation by the photocatalytic reaction is 0.0126.

The photocatalytic degradation of DCIP in aqueous suspension of TiO_2 was repeated with titanium dioxide with an unknown surface area produced in CSFR.

It was found that TiO_2 (rutile) is photocatalytically inactive. During the 60 min exposition no changes of the DCIP solution concentration were determined and the solution pH values were changed only slightly (Fig. 6, curve *3*).

The suspension colour change from blue to pink and to white was observed by the photocatalytic decomposition of the DCIP aqueous suspension of TiO_2 (anatase). The decomposition rate constant is about 10 times lower than that in the system with the same amount of TiO_2 (P25) (Table 1, Fig. 8). The significant pH values decrease is observed during irradiation (Fig. 6, curve *2*). The photocatalytic activity of this anatase is lower, carbon skeleton oxidation is delayed after dechlorination and therefore CIP and IP spots were observed on TLC irradiated samples, too.

Photocatalytic decomposition of DCIP *on* TiO_2 (P25) *by solar radiation*

The photocatalytic decomposition of the DCIP aqueous solution on TiO_2 (Fig. 9, curve *2*) and on Pt (2 mass %)/TiO_2 (P25) (Fig. 9, curve *3*) was observed

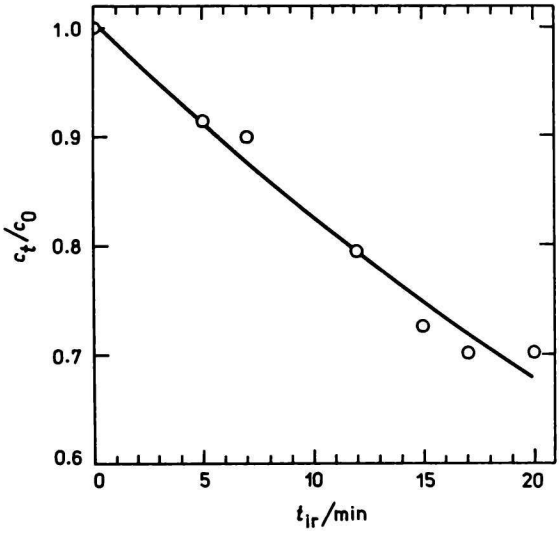


Fig. 8. The changes of the relative DCIP concentration during photocatalytical degradation on TiO_2 (anatase). 0.5 g TiO_2/100 g DCIP solution.

during solar radiation as well. The 99 % decomposition was observed after 12 h irradiation of the suspension in the closed vessels, made of thin laboratory glass, located on the reflective background in direct solar light. The concentration of DCIP solution without TiO_2 was not changed during the solar radiation exposition (Fig. 9, curve *1*).

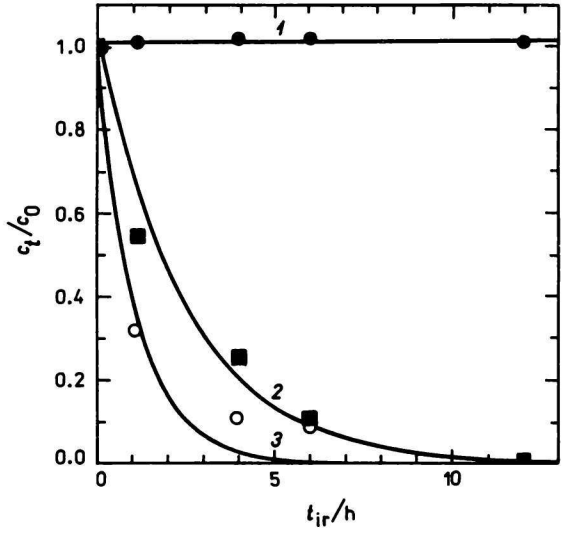


Fig. 9. The changes of the relative DCIP concentration during photocatalytical degradation on TiO_2 (P25) by solar radiation. *1.* Without TiO_2; *2.* 0.4 g TiO_2/100 g DCIP solution; *3.* 0.4 g Pt (2 mass %)/ /TiO_2/100 g DCIP solution.

Conclusion

Experimental results can be summarized as follows:

1. DCIP is photocatalytically oxidized on the active TiO_2 surface by the medium pressure Hg lamp with pyrex sleeve irradiation ($\lambda > 280$ nm). 95 % DCIP decomposition was observed after 20 min irradiation at optimal conditions.

2. Photocatalytic decomposition of DCIP in aqueous suspension of TiO_2 can be described by formal first-order kinetics.

3. The same results were obtained for TiO_2 (P25) by Hg lamp irradiation and solar exposure as well.

4. According to supposed mechanism, carboxylic acids are formed during the photocatalytic oxidation. This is accompanied by significant pH values decrease, and consequently the DCIP solution colour is changed (acid-base indicator) [37]. The reaction is suitable for testing the semiconductor powder photocatalytic activity.

Acknowledgements. We are very grateful to Degussa (FRG) for kindly granting TiO_2 (P25) *sample.*

References

1. Willner, I. and Steinberger-Willner, B., *Int. J. Hydrogen Energy 13,* 593 (1988).
2. Bard, A. J., *J. Electroanal. Chem. Interfacial Electrochem. 168,* 5 (1984).
3. Weber, M. F. and Dignam, M. J., *J. Electrochem. Soc. 131,* 1258 (1984).
4. Sakata, T. and Kawai, T., *Nouv. J. Chim. 5,* 279 (1981).
5. Kawai, T. and Sakata, T., *Nature 286,* 474 (1980).
6. Kawai, T. and Sakata, T., *J. Chem. Soc., Chem. Commun. 1980,* 694.
7. Endoh, E. and Bard, A. J., *Nouv. J. Chim. 11,* 217 (1987).
8. Kudo, A., Domen, K., Maruya, K., and Onishi, T., *Chem. Lett. 1987,* 1019.
9. Miyama, H., Nosaka, Y., Fukushima, T., and Toi, H., *J. Photochem. 36,* 121 (1987).
10. Anpo, M., Aikawa, N., and Kubokawa, Y., *J. Phys. Chem. 88,* 3998 (1984).
11. Matthews, R. W., *J. Phys. Chem. 91,* 3328 (1987).
12. Matthews, R. W., *J. Chem. Soc., Faraday Trans. 1 80,* 457 (1984).
13. Hustert, K. and Moza, P. N., *Chemosphere 17,* 1751 (1988).
14. Matthews, R. W., *Sol. Energy 38,* 405 (1987).
15. Ollis, D. F., *Environ. Sci. Technol. 19,* 480 (1985).
16. Hidaka, H., Yamada, S., Suenaga, S., Kubota, H., Serpone, N., Pelizzetti, E., and Graetzel, M., *J. Photochem. Photobiol. A 47,* 103 (1989).
17. Tennakone, K., Punchihewa, S., and Tantrigoda, R. U., *Environ. Pollut. 57,* 299 (1989).
18. Matthews, R. W., *J. Catal. 113,* 549 (1988).
19. Kalyanasundaram, K., in *Semiconductor Particulate System for Photocatalysis and Photosynthesis in Energy Resources through Photochemistry and Catalysis.* (Graetzel, M., Editor.) Academic Press, London, 1983.

20. Lapčík, L., Pelikán, P., and Čeppan, M., *Fotochemické procesy.* (Photochemical Processes.) Alfa Publishers, Bratislava, 1989.
21. Pichat, P., in *Photocatalytic Reactions in Photoelectrochemistry, Photocatalysis and Photoreactors.* (Schiavello, M., Editor.) D. Reidel Publishing Company, New York, 1985.
22. Pollert, E., *Czech. J. Phys., A 34,* 258 (1984).
23. Wong, M. K. and Malati, M. A., *Sol. Energy 36,* 163 (1983).
24. Day, R. E. and Egerton, T. A., *Colloids Surf. 23,* 137 (1987).
25. Bahnemann, D. W., Henglein, A., Lilie, J., and Spanhel, L., *J. Phys. Chem. 88,* 709 (1984).
26. Hermann, J.-M., Pichat, P., and Disdier, J., *Chem. Phys. Lett. 108,* 618 (1984).
27. Kraeutler, B. and Bard, A. J., *J. Am. Chem. Soc. 100,* 5985 (1978).
28. Kormann, C., Bahnemann, D. W., and Hoffmann, M. R., *J. Photochem. Photobiol. A 48,* 161 (1989).
29. Kraeutler, B. and Bard, A. J., *J. Am. Chem. Soc. 100,* 4317 (1978).
30. Sakata, T., Kawai, T., and Hashimoto, K., *Chem. Phys. Lett. 88,* 50 (1982).
31. Rabek, J. F., *Experimental Methods in Photochemistry and Photophysics.* J. Wiley & Sons, Chichester—New York, 1982.
32. Gasparič, J. and Churáček, J., *Papírová a tenkovrstvá chromatografie organických sloučenin.* (Paper and Thin-Layer Chromatography of Organic Compounds.) Nakladatelství technické literatury (Publishers of Technical Literature), Prague, 1981.
33. Murov, S. L., *Handbook of Photochemistry.* M. Dekker, New York, 1973.
34. Veselý, M., *PhD. Thesis.* Slovak Technical University, Bratislava, 1988.
35. Matthews, R. W., *J. Chem. Soc., Faraday Trans. 1 85,* 1291 (1989).
36. Salvador, P. and Gutierrez, C., *J. Phys. Chem. 88,* 3696 (1984).
37. Patrick, R. A. and Svehla, G., *Anal. Chim. Acta 88,* 363 (1977).

Translated by D. Marianiová