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Solvent effect on the photocatalytic reduction of 4-nitrophenol in titanium dioxide suspensions

V. Brezová *, A. Blažková, I. Šurina, B. Havlínová

Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

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Abstract

The selective photocatalytic reduction of 4-nitrophenol to 4-aminophenol in titanium dioxide suspensions prepared in aliphatic alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, *i*-butanol) was investigated. The photoreduction rate is significantly affected by the solvent parameters, such as viscosity, polarity, polarisability, and polarity/polarisability. © 1997 Elsevier Science S.A.

Keywords: Titanium dioxide; Photocatalytic reduction; 4-Nitrophenol; Solvent effect

1. Introduction

The photochemical electron and hydrogen transfers in aromatic nitro compounds attract the attention of photochemists, and the individual steps in the photoinduced reactions were studied in details [1–5]. However, some nitro compounds, e.g., nitrophenols are photoresistant both to photoreduction and photosubstitution reactions. This is related to the state with the charge transfer's large contribution to their excited state [4,5].

The effective reduction of aromatic and aliphatic nitro compounds was performed in the irradiated TiO_2 suspensions [6]. Especially, the reduction efficiency relating to the reduction potentials of nitro compounds [7], allowed the selective reduction of the nitro group in the multifunctional compounds [8].

Illumination of semiconducting TiO_2 particles by the supra-band gap irradiation causes the formation of charge carriers; the positive holes (h^+) are generated in the valence band and the negative electrons (e^-) in the conduction band of semiconductor. After separation, the photogenerated charge carriers may be involved in the redox processes on the TiO_2 surface [9–12].

The electrons in the conduction band of TiO_2, characterized by the reduction potential of $E_{cb} = -0.80$ V vs. SCE in acetonitrile [9–12], are readily available for the transfer to an electron acceptor (A) with the appropriate value of reduction potential $E_{A/A^{-\bullet}}$ [9–12].

$$TiO_2 + h\nu \rightarrow TiO_2(e^- + h^+) \quad (1)$$

$$e^- + A \rightarrow A^{-\bullet} \quad (2)$$

The driving force for the heterogeneous electron transfer is the energy difference between the conduction band of semiconductor and the reduction potential of the acceptor redox couple $A/A^{-\bullet}$ [13]:

$$\Delta E = E_{cb} - E_{A/A^{-\bullet}} \quad (3)$$

Similarly, the holes in the TiO_2 valence band with an oxidation potential of 2.4 V vs. SCE in acetonitrile [9–12] are open for the electron donation from the suitable electron donor, D [14,15]:

$$h^+ + D \rightarrow D^{+\bullet} \quad (4)$$

Alcohols applied as a solvent are oxidized during irradiation by the photogenerated holes to carbonyl compounds [16,17] via radical intermediates formed by abstracting hydrogen atom from the position α to the hydroxyl group of individual alcohols [18].

$$R\text{–}CH_2\text{–}OH + h^+ \rightarrow R\text{–}{}^{\bullet}CH\text{–}OH + H^+ \quad (5)$$

$$R\text{–}{}^{\bullet}CH\text{–}OH \rightarrow R\text{–}COH + \cdot H \quad (6)$$

$$2 \cdot H \rightarrow H_2 \quad (7)$$

According to the reaction mechanism proposed by Mahdavi et al. [6] for the reduction of nitro compounds in the irradiated alcoholic TiO_2 suspensions (Eq. (8)), the reduction efficiency is influenced by a series of processes and factors including the electron transfer from the conduction

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* Corresponding author. E-mail: brezova@cvtstu.cvt.stuba.sk

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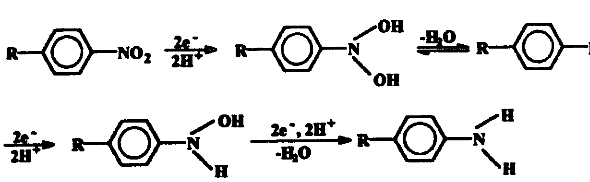
band of TiO_2 to a nitro compound, the back-electron transfer from a nitro radical anion to the valence band, and proton availability [6].



(8)

In the paper presented, we investigated the photocatalytic reduction of 4-nitrophenol sensitized by TiO_2 using six aliphatic alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and *i*-butanol) as solvent, and the influence of their properties on the photocatalytic process were evaluated.

2. Experimental

2.1. Materials

Titanium dioxide P25 (Degussa, Germany) was used in all photocatalytic experiments in a concentration of 1 g dm^{-3}. Degussa P25 is a non-porous 70:30% anatase-to-rutile mixture with a BET surface area of 55 ± 15 m^2 g^{-1} and crystallite sizes of 30 nm in 0.1 μm diameter aggregates [19].

The solvents used, methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), 1-butanol (1-BuOH) and *iso*-butanol (*i*-BuOH), were purchased in quality for UV spectroscopy from Lachema (Czech Republic). 4-Nitrophenol (4-NP) and 4-aminophenol (4-AP) of analytical grade were obtained from Aldrich.

2.2. Apparatus and procedures

The alcoholic suspensions (4 ml) containing 1 mM of 4-nitrophenol were thoroughly purged with nitrogen before irradiation, and during exposure a slight nitrogen stream was introduced in the quartz rectangular cell with graded seal (cell length 10 mm). The cell was thermostatically controlled at 25 ± 1 °C. The TiO_2 powder was removed from samples before analysis by means of MLW (T62.2, Germany) centrifuge.

A Narva (HBO 500, Germany) high-pressure mercury lamp served as an irradiation source (radiation flux of 6×10^{-9} mol s^{-1}). The emission line with wavelength 365 nm was selected by a combination of UG1 and WG360 filters.

The UV spectra were monitored using Philips (PU 8800) UV–vis. spectrophotometer; quartz cell (length 1 mm) was used.

The IR spectra were measured by means of a Perkin Elmer (599) IR spectrometer. The following technique of sample preparation was used: KBr powder was dipped in the ethanolic 4-nitrophenol irradiated solution (TiO_2 powder was removed by centrifugation). The sample was dried at 30 °C under vacuum for 6 h. The KBr pellets were pressed for measuring the IR spectra, instantly.

The identification of photoreduction products was performed by means of a Hewlett–Packard (5980A/5790) gas chromatograph–mass spectrometer (GC–MS). The conditions of the GC–MS analysis were as follows: column ULTRA-1; length, 25 m; internal diameter, 0.2 mm; film, 0.33 μm; temperature programme, 40 °C (4 min), heated at 10 °C min^{-1} to 250 °C (5 min); carrier, helium 1 ml min^{-1}; CHP (column head pressure) = 50 kPa; TF (total flow) = 50 ml; injector temperature, 250 °C; interface to MSD HP5970B capillary direct; mass spectral range 42–400 amu; threshold 1000; electron impact 2200 V.

The concentrations of 4-nitrophenol and its main reduction product, 4-aminophenol, were determined using high-performance liquid chromatography (HPLC) by means of FPLC (Pharmacia, Sweden) apparatus, applying a Separon SIX C-18 column (Tessek, Czech Republic) and UV detector ($\lambda = 280$ nm). A mixture of methanol:water:H_3PO_4 (35:65:0.1) was selected as the optimal mobile phase for the samples in MeOH, EtOH, 1-PrOH, 2-PrOH and (65:35:0.1) for 1-BuOH and *i*-BuOH solutions. For all solvents, the calibration curves were measured and evaluated to determine 4-nitrophenol and 4-aminophenol concentrations.

3. Results and discussion

Fig. 1 represents the changes observed in the UV spectra during 365 nm irradiation of 1 mM 4-nitrophenol in TiO_2 methanol suspension. The characteristic absorption band of 4-nitrophenol, which is hypsochromically shifted in the region about 312 nm, due to the acidic character of TiO_2 methanol suspension, vanished by 365 nm exposure, and a new absorption peak at 241 nm is formed.

The IR spectrum obtained for 1 mM 4-nitrophenol ethanol suspension irradiated 30 min is depicted in Fig. 2. Its com-

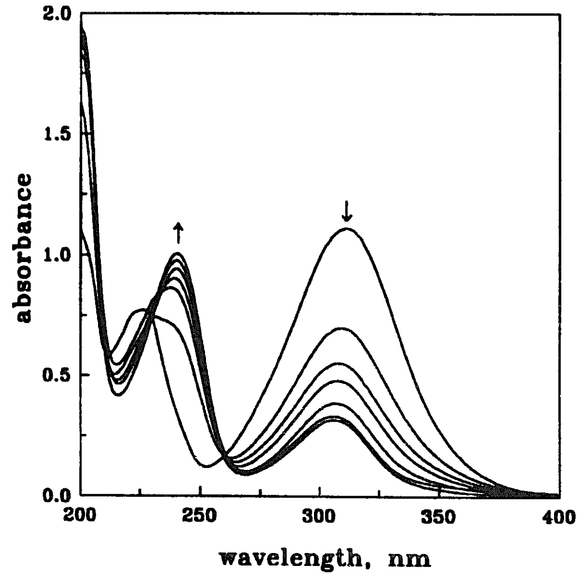


Fig. 1. Changes in UV spectra observed during irradiation ($\lambda = 365$ nm) of 1 mM 4-nitrophenol in methanol TiO_2 suspension ($c_{TiO_2} = 1$ g dm^{-3}). Irradiation times: 0, 4, 6, 8, 10, 15 and 20 min. Cell length 1 mm.

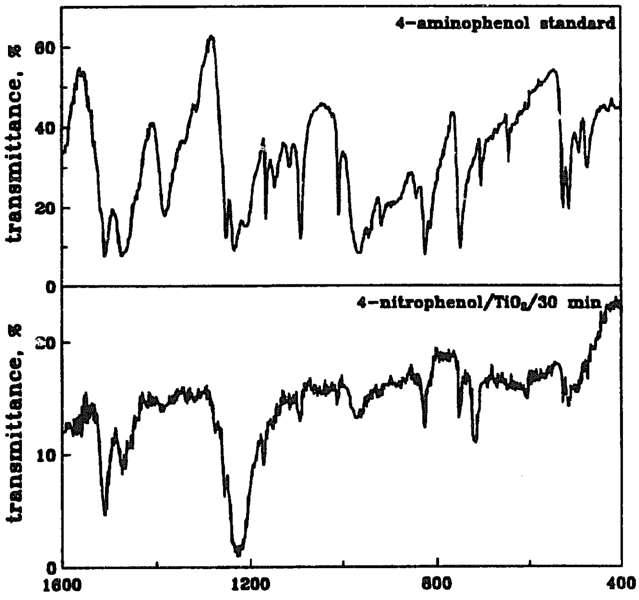


Fig. 2. IR spectrum measured for 1 mM 4-nitrophenol irradiated ($\lambda = 365$ nm) 30 min in ethanol TiO_2 suspension ($c_{TiO_2} = 1$ g dm^{-3}) in comparison with IR spectrum obtained for 4-aminophenol standard using KBr technique.

parison with the IR spectrum of original 4-aminophenol sample exhibits good agreement in the characteristic 4-aminophenol vibrations at 1510, 1475, 1385, 1255, 1235, 1095, 1012, 970, 825 and 750 cm^{-1}.

Moreover, the unambiguous identification of the reaction products offers GC–MS analysis. Only one product, 4-aminophenol, was found in the irradiated TiO_2 suspensions containing 4-nitrophenol. Under given experimental conditions, the retention times were 16.5 min for 4-nitrophenol and 12.7 min for 4-aminophenol, respectively. 4-Aminophenol was produced neither in dark, nor under 365 nm illumination without TiO_2.

The decrease in 4-nitrophenol concentration and the formation of 4-aminophenol during irradiation in the methanol TiO_2 suspensions is shown in Fig. 3. The kinetic curves obtained in all solvents are characteristic for the formal first-order kinetics, and were fitted to the exponential function:

$$c = A + B\exp(-k \times t_{irr}) \tag{9}$$

where t_{irr} is irradiation period, c is the concentration of 4-nitrophenol or 4-aminophenol in samples, k is formal first-order rate constant of 4-NP decrease or 4-AP formation, and A, B are constants.

The formal first-order rate constants, $k_{4\text{-NP}}$ and $k_{4\text{-AP}}$, thus calculated for TiO_2 photosensitized reaction in different alcohols (see Table 1), are significantly influenced by the solvent. The best yield of 92% was obtained after 20 min irradiation ($\lambda = 365$ nm) of 4-nitrophenol in methanol suspensions (Fig. 3).

Langmuir–Hinshelwood (LH) and Eley–Rideal (ER) kinetic models as well as their combinations were successfully applied in the kinetic analysis of various semiconductor-induced photoreaction as summarized in Refs. [9,10].

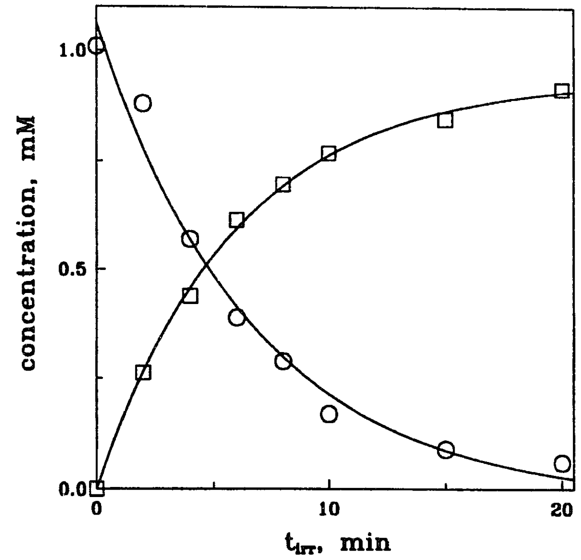


Fig. 3. Concentration changes of 4-nitrophenol (○) and 4-aminophenol (□) during 365 nm irradiation in methanol TiO_2 suspension ($c_{TiO_2} = 1$ g dm^{-3}).

Table 1
The formal first-order rate constants in TiO_2 alcoholic suspensions calculated from the dependencies of 4-nitrophenol and 4-aminophenol concentration on irradiation time

Solvent	$k_{4\text{-NP}}$ (min^{-1})	$k_{4\text{-AP}}$ (min^{-1})
Methanol	0.154	0.168
Ethanol	0.106	0.095
1-Propanol	0.091	0.073
2-Propanol	0.063	0.050
1-Butanol	0.048	0.050
i-Butanol	0.017	0.012

If both Langmuir–Hinshelwood and Eley–Rideal reaction pathways are actual, then the overall rate of 4-nitrophenol reduction can be described as:

$$R = k_{ER}c_{4\text{-NP}} + \frac{k_{LH}K'c_{4\text{-NP}}}{1 + K'c_{4\text{-NP}}} \tag{10}$$

where k_{ER} and k_{LH} are the Eley–Rideal and Langmuir–Hinshelwood reaction rate constants, $K' = K/4-NP/1 + K_S c_S$, $K_{4\text{-NP}}$ and K_S are adsorption constants of 4-NP and solvent, $c_{4\text{-NP}}$ is the initial concentration of 4-NP and c_S is the concentration of solvent.

The effect of 4-nitrophenol initial concentration on the rate of 4-aminophenol formation in methanol is depicted in Fig. 4. The experimental data were fitted by the function

$$R = 0.55c_{4\text{-NP}} + \frac{0.19c_{4\text{-NP}}}{1 + 4.4c_{4\text{-NP}}} \tag{11}$$

which is in accordance with Eq. (10). The experimental data obtained imply that both LH and ER pathways contribute to the production of 4-aminophenol. The rate constants ratio $k_{ER}/k_{LH} \sim 13$ indicates that the ER mechanism is favoured.

As solvent properties can substantially affect the electron transfer kinetics, in the further study we attempted to correlate

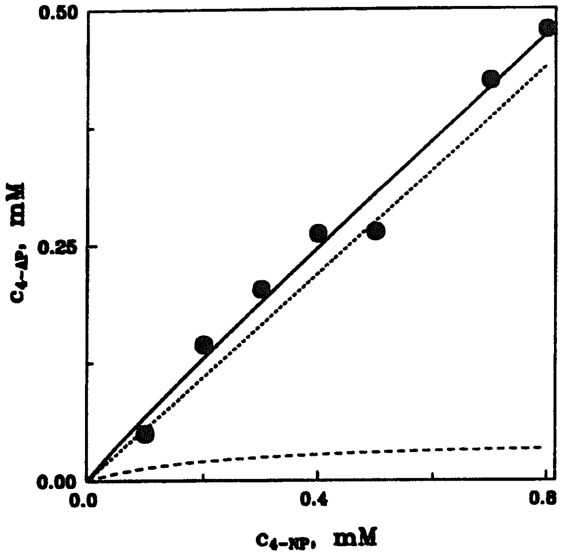


Fig. 4. The effect of initial concentration of 4-nitrophenol on the rate of 4-aminophenol formation in methanol. The samples were irradiated 10 min (λ = 365 nm, temperature 25 °C). The overall rate (———) calculated using Eq. (11) is separated into ER contribution (· · ·) and LH contribution (- - -).

the rate of 4-nitrophenol reduction photosensitized by TiO_2, with some selected solvent parameters, such as:

(1) Viscosity;

(2) Solvent polarity [20]

$$Y=(\epsilon_s-1)/(\epsilon_s+2) \tag{12}$$

where ϵ_S is relative solvent permittivity.

(3) Solvent polarisability [20]

$$P=(n^2-1)/(n^2+2) \tag{13}$$

where n is the solvent refractive index for the sodium D-line.

(4) Solvent polarity/polarisability parameter π^*, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect [21,22].

The data for the six alcohols used in our study are summarized in Table 2.

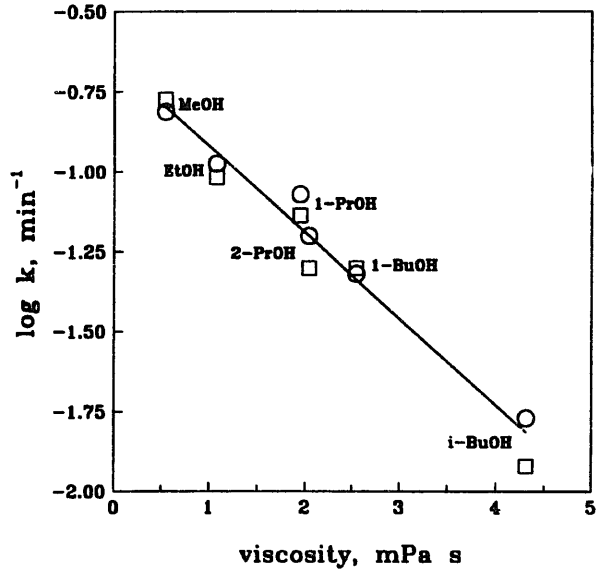


Fig. 5. Dependence of the logarithm of the formal first-order rate constant in the TiO_2 photosensitized reduction of 4-nitrophenol (○) to 4-aminophenol (□) on the solvent viscosity.

The solvent viscosity, η, significantly influenced the rate of 4-nitrophenol photoreduction on TiO_2, and the linear dependence $\log k = -0.65 - 0.27\eta$ ($R^2 = 0.96$) was obtained (Fig. 5). Due to the differences in values of $k_{4\text{-PN}}$ and $k_{4\text{-AP}}$ evaluated from the exponential curves (Table 1), the appropriateness to use together $k_{4\text{-PN}}$ and $k_{4\text{-AP}}$ in one common data set was tested and confirmed before all correlation calculations.

Table 2
The parameters of solvents used in the study

Solvent	η (mPa s) [a]	ϵ_S [b]	n [c]	π^* [d]
Methanol	0.544	32.66	1.326	0.60
Ethanol	1.074	24.3	1.359	0.54
1-Propanol	1.945	20.1	1.383	0.52
2-Propanol	2.038	18.3	1.375	0.48
1-Butanol	2.544	17.1	1.397	0.47
i-Butanol	4.312	17.7	1.394	0.40

[a] Viscosity at 25 °C, Ref. [23].
[b] Relative solvent permittivity at 25 °C, Ref. [24].
[c] Solvent refractive index at 25 °C, Ref. [25].
[d] Polarity/polarisability taken from Ref. [22].

According to the Stokes–Einstein equation

$$D=kT/6\pi r\eta \tag{14}$$

where D is the diffusion coefficient and r is the radius of the diffusing species approximated by a sphere [20], the solvent viscosity may influence the diffusion of reaction intermediates to/from the irradiated TiO_2 surface. As the TiO_2 photosensitized reduction of 4-nitrophenol to 4-aminophenol is a complex process with sequential electron transfers, protona-

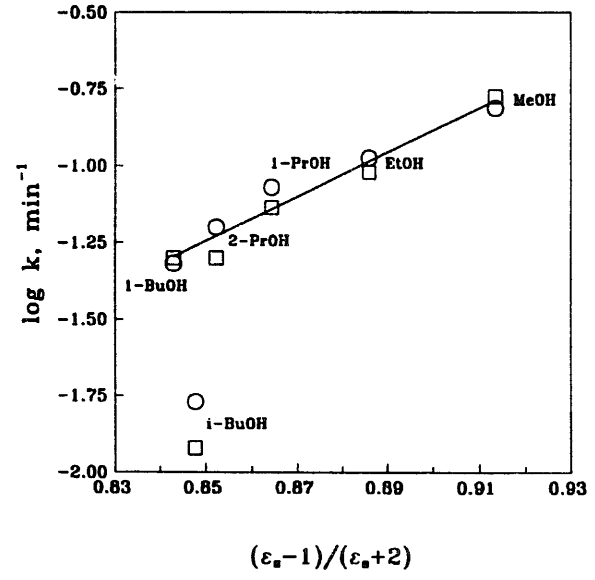


Fig. 6. Dependence of the logarithm of the formal first-order rate constant in the TiO_2 photosensitized reduction of 4-nitrophenol (○) to 4-aminophenol (□) on the solvent polarity parameter, $Y=(\epsilon_S-1)/(\epsilon_S+2)$.

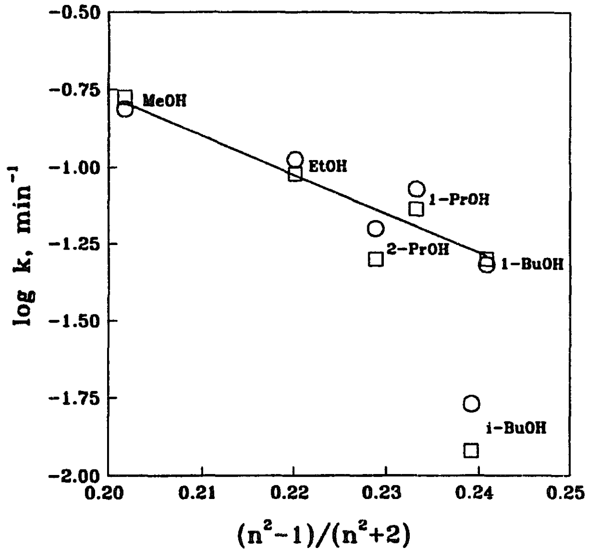


Fig. 7. Dependence of the logarithm of the formal first-order rate constant in the TiO_2 photosensitized reduction of 4-nitrophenol (○) to 4-aminophenol (□) on the solvent polarisability parameter, $P=(n^2-1)/(n^2+2)$.

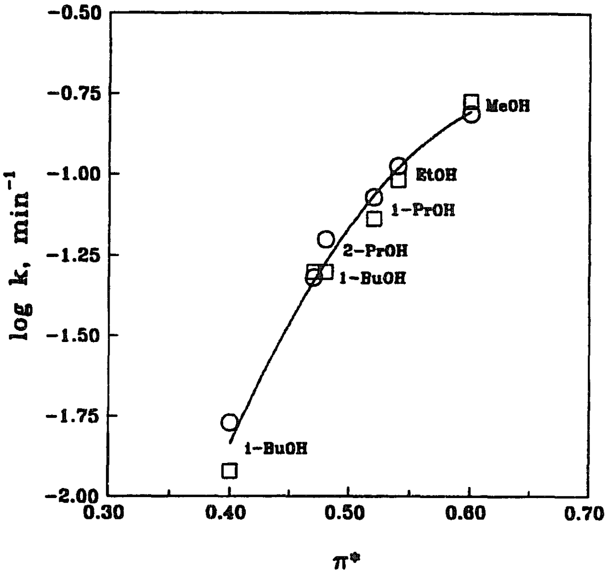


Fig. 8. Dependence of the logarithm of the formal first-order rate constant in the TiO_2 photosensitized reduction of 4-nitrophenol (○) to 4-aminophenol (□) on the solvent polarity/polarisability parameter, π^*.

tions and dehydration, the influence of the solvent reorientation dynamics [26–28] on the reaction rate is not considered here.

The rate of photosensitized reduction increased with increasing polarity of solvent, as depicted in Fig. 6. Except *i*-BuOH, the linear dependence $\log k = -7.37 + 7.2Y$ ($R^2 = 0.94$) was found. In the polar solvents the back electron transfer from nitro radical anions to TiO_2 valence band is probably suppressed, which is reflected in the higher values of the formal first-order constants obtained in methanol and ethanol (Table 1).

Additionally, the influence of solvent polarisability P on the reaction rate was observed (Fig. 7). However, again significant deviation from linear behaviour was observed for *i*-butanol solvent as can be seen in Figs. 6 and 7.

Very good correlation was obtained for the polarity–polarisability parameter π^* as shown in Fig. 8. The photoreduction rate increases quadratically with increasing the π^* values of solvents, $\log k = -7.7 + 21.0\pi^* - 15.8(\pi^*)^2$ ($R^2 = 0.98$).

Finally, it can be concluded that the ability of solvent to stabilize the charged intermediate species produced, plays an important role in TiO_2 photosensitized reduction of 4-nitrophenol in alcohol solvents.

Acknowledgements

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References

[1] N.J. Turro, Modern Molecular Photochemistry (Benjamin/Cummings, Menlo Park, CA, 1978) p. 393.
[2] L'. Lapčík, P. Pelikán, M. Čeppan, Photochemical Processes (Alfa, Bratislava, 1989) p. 205.
[3] W.M. Horspool, Aspects of Organic Photochemistry (Academic Press, New York, 1976).
[4] D. Dorr, Topics Curr. Chem. 55 (1975) 49.
[5] J. Malkin, Photophysical and Photochemical Properties of Aromatic Compounds (CRC, Boca Raton, 1992) p. 219.
[6] F. Mahdavi, T.C. Bruton, Y. Li, J. Org. Chem. 58 (1993) 744.
[7] J.A Dean (ed.), Handbook of Organic Chemistry (McGraw-Hill, New York, 1987) Section 8.
[8] C. Joyce-Pruden, J.K. Pross, Y. Li, J. Org. Chem. 57 (1992) 5087.
[9] H. Al-Ekabi, N. Serpone, in: N. Serpone, E. Pelizzetti (eds.), Photocatalysis. Fundamentals and Applications (Wiley, New York, 1989) p. 457.
[10] H. Al-Ekabi, in: V. Ramamurthy (ed.), Photochemistry in Organized and Constrained Media (VCH, New York, 1991) p. 495.
[11] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.
[12] P.V. Kamat, Chem. Rev. 93 (1993) 267.
[13] A.L. Linsebigler, G. Lu, J.T. Yates, Jr., Chem. Rev. 95 (1995) 735.
[14] J.L. Muzyka, M.A. Fox, J. Org. Chem. 55 (1990) 209.
[15] E. Baciocchi, G.C. Rosato, C. Rol, G.V. Sebastiani, Tetrahedron Lett. 33 (1992) 5437.
[16] E. Borgarello, E. Pelizzetti, Chim. Ind. 65 (1983) 474.
[17] S. Teratani, J. Nakamichi, K. Taya, K. Tanaka, Bull. Chem. Soc. Jpn. 55 (1982) 1688.
[18] M. Kaise, H. Nagai, K. Tokuhashi, S. Kondo, S. Nimura, O. Kikuchi, Langmuir 10 (1994) 1345.
[19] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[20] M. Hecht, W.R. Fawcett, J. Phys. Chem. 99 (1995) 1311.
[21] M.J. Kamlet, J.-L.M. Abboud, M.H. Abraham, R.W. Taft, J. Org. Chem. 48 (1983) 2877.
[22] Y. Marcus, Chem. Soc. Rev. 22 (1993) 409.
[23] D.R. Lide (ed. in chief), Handbook of Chemistry and Physics. 74th Edn., 1993-1994 (CRC, Boca Raton, 1993) p. 6–193.
[24] D.R. Lide (ed. in chief), Handbook of Chemistry and Physics. 74th Edn, 1993-1994 (CRC, Boca Raton, 1993) p. 6–148.
[25] D.R. Lide (ed. in chief), Handbook of Chemistry and Physics. 74th Edn., 1993-1994 (CRC, Boca Raton, 1993) p. 3–634.
[26] P.J. Reid, P.F. Barbara, J. Phys. Chem. 99 (1995) 3554.
[27] M. Opallo, J. Chem. Soc., Faraday Trans. 1 82 (1986) 339.
[28] R. Chen, G.R. Freeman, J. Phys. Chem. 99 (1995) 4970.