Monatshefte für Chemie 130, 377–384 (1999)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Photocatalysis by Illuminated Titania: Oxidation of Hydroquinone and *p*-Benzoquinone

Andrzej Sobczyński*, **Łukasz Duczmal,** and **Anna Dobosz**

Faculty of Commodity Science, Poznań University of Economics, PL-60067 Poznań, Poland

Summary. Photocatalytic oxidation of hydroquinone and *p*-benzoquinone, the main intermediates which are formed in the process of phenol oxidation on irradiated titania, was studied. The reaction proceeds *via* several steps. Some of the intermediates were detected by HPLC and GC-MS: ethanedial, glycerol, and 1,2,4-trihydroxybenzene. Under illumination in the presence of TiO_2, *p*-benzoquinone initially transforms partly to hydroquinone, partly oxidizes to unidentified intermediates. The residue, about 4% of the concentration of hydroquinone, undergoes slow oxidation together with the hydroquinone. The rate of hydroquinone photooxidation shows 1st order behaviour.

Keywords. Photodegradation; Hydroquinone; *p*-Benzoquinone; Intermediates; Kinetics.

Photokatalyse durch belichtetes TiO_2: Oxidation von Hydrochinon und *p*-Benzochinon

Zusammenfassung. Die Photokatalyse von Hydrochinon und *p*-Benzochinon, den wesentlichsten Zwischenprodukten bei der Oxidation von Phenol an belichtetem TiO_2, wurde untersucht. Die Reaktion verläuft über mehrere Stufen. Einige der Zwischenprodukte konnten mittels HPLC und GC-MS nachgewiesen werden: Ethandial, Glycerin und 1,2,4-Trihydroxybenzol. Unter Lichteinwirkung in Gegenwart von TiO_2 setzt sich *p*-Benzochinon zuerst teilweise zu Hydrochinon um, teilweise wird es zu nicht identifizierten Produkten oxidiert. Der Rückstand (*ca.* 4% der Menge an Hydrochinon) wird zusammen mit Hydrochinon langsam weiter oxidiert. Die Kinetik der Photooxidation von Hydrochinon verläuft nach erster Ordnung.

Introduction

If a semiconductor, *e.g.* TiO_2, is illuminated by light with a wavelength equal or higher than its forbidden gap, electrons and holes are generated on and near the surface. Some of the electron-hole pairs recombine, some are trapped into the so-called surface traps giving highly active surface species (Ti^{3+} and O^- or $^{\cdot}OH$) [1, 2]. In aqueous TiO_2 suspensions saturated with air or oxygen, hydroxyl radicals are mainly formed [3, 4]. They attack organic molecules present in the solution forming organic radicals which can react further with photogenerated electrons or holes or primary products of their reactions giving highly oxidized species; the

---

* Corresponding author

final products are carbon dioxide and water. The trapped electrons react mainly with molecular oxygen dissolved in water. As a result, surface O_2^- is formed; this ion can be reduced further to H_2O_2, $^{\cdot}OH$, and OH^- [2]. The produced species may react with the organic radicals formed in the oxidative route. Therefore, the organic compounds present in the illuminated titania slurry undergo many chain, consecutive, and other reactions [2, 4–11]. Finally, in an ideal case, all intermediate compounds are fully mineralized, *i.e.* they are oxidized to carbon dioxide and water.

Although photodecomposition of phenol in aerated aqueous TiO_2 suspensions leads finally to CO_2 and H_2O, a number of aromatic [12] and aliphatic [13] intermediates are also obtained. Recent investigations have shown a big difference between phenol and total organic carbon diminution [14], confirming thus the existence of a number of reaction intermediates. Most recent studies on photocatalytic oxidation of phenol on illuminated TiO_2 show that several ring intermediates like di- and trihydroxybenzenes are present in the reaction mixture [15]. It has also been observed that hydroquinone and *p*-benzoquinone are the major intermediates of the process. The present paper deals with the photocatalytic oxidation of these compounds.

Results and Discussion

As has been mentioned above, hydroquinone and *p*-benzoquinone are the main ring intermediates formed in the photocatalytic oxidation of phenol in the presence of TiO_2. Quantitatively, about 15% hydroquinone and 4% *p*-benzoquinone (initial phenol concentration: $2 \cdot 10^{-4}\,M$) were detected after 3 hours of the photocatalytic reaction [15]. Therefore, the photocatalytic phenol oxidation obviously follows mainly the pathway phenol → hydroquinone (*HQ*) → *p*-benzoquinone (*BQ*) → other intermediates.

It is well known from the chemistry of hydroquinone and *p*-benzoquinone that both compounds can be easily transformed into one another [16, 17]; the normal redox potential of *BQ*/*HQ* amounts to 0.715 V [18]. Also, both compounds may undergo further hydroxylation [16, 17]. Irradiation of *HQ* and *BQ* solutions ($\lambda = 254$ nm) can yield coupled products, *e.g.* 2,2′,5,5′-tetrahydroxybiphenyl [17].

The results of the photocatalytic oxidation of $2 \cdot 10^{-4}\,M$ solutions of *HQ*, *BQ* and, in addition, an equimolar mixture of both compounds, are shown in Figs. 1–3. Three techniques were applied in order to follow the disappearance of the compounds: their total oxidation, *i.e.* their mineralization to CO_2 and H_2O, was studied by means of total organic carbon measurements (TOC), formation of intermediates, HPLC, and GC-MS.

It can be seen from Figs. 1–3 that in all solutions *HQ* and *BQ* are present, although at different proportions. The *HQ* solution contains initially about 4% *BQ* (Fig. 1). When illuminated, both compounds underwent decomposition; after 3 h their concentrations were lowered by about 2.5 times (Fig. 1). It is worth mentioning that under the conditions of the photocatalytic reaction the ratio *BQ*/(*BQ*+*HQ*) was nearly constant: the slurry still contained 4–5% *BQ*. If one assumes that oxidation of hydroquinone yields primarily *p*-benzoquinone (see above), it is clear that the last compound undergoes fast transformations resulting in a constant

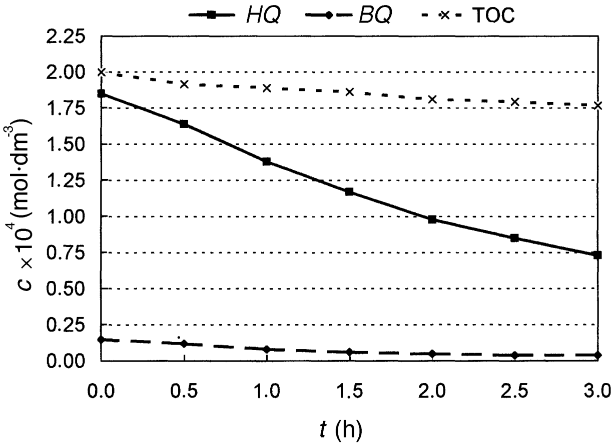

Fig. 1. Changes in the reaction solution *vs.* time during photocatalytic oxidation of hydroquinone; the loss of TOC is expressed in units of hydroquinone (and *p*-benzoquinone) concentration

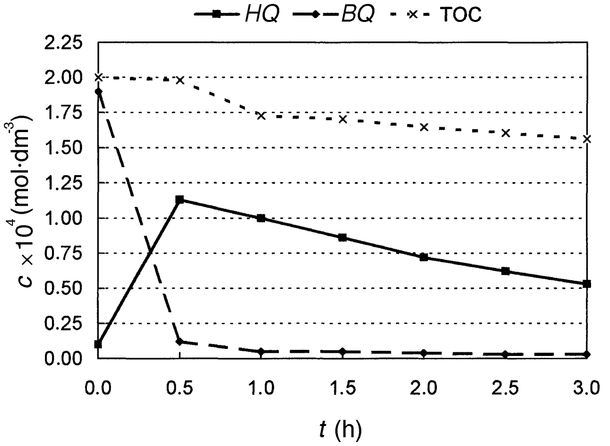

Fig. 2. Changes in the reaction solution *vs.* time during photocatalytic oxidation of *p*-benzoquinone; the loss of TOC is expressed in units of *p*-benzoquinone (and hydroquinone) concentration

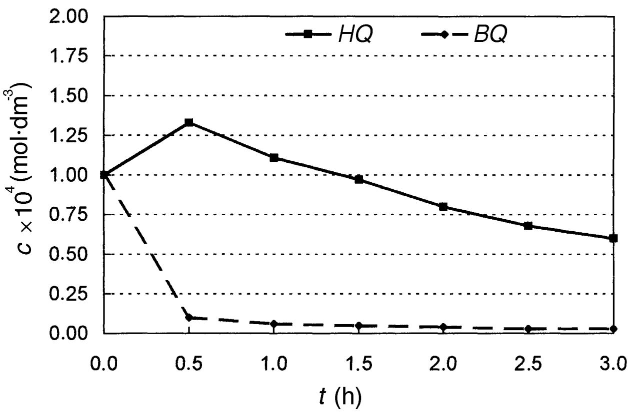

Fig. 3. Changes in the reaction solution *vs.* time during photocatalytic oxidation of a 1:1 hydroquinone/*p*-benzoquinone mixture

BQ/(*BQ*+*HQ*) ratio. Mineralization of the reaction mixture, *i.e.* oxidation to CO_2 and H_2O, proceeds much slower: after 3 h of illumination, only about 14% of initial organic matter (*BQ*+*HQ*) disappeared (see the TOC curve in Fig. 1).

The picture of the photocatalytic *BQ* oxidation is somewhat more complicated (Fig. 2). Initially, the concentration of *BQ* in the reaction slurry was about $1.83 \cdot 10^{-4} M$, that of *HQ* $0.17 \cdot 10^{-4} M$ (about 9% *HQ*). As before, the total concentration was $2 \cdot 10^{-4} M$. However, after 30 min illumination the concentrations of *BQ* and *HQ* were $0.05 \cdot 10^{-4} M$ and $1.13 \cdot 10^{-4} M$. Note that (*i*) the amount of *BQ* decreased drastically, (*ii*) at the same time the amount of *HQ* increased strongly, although to a lesser extent, and (*iii*) the ratio *BQ*/(*BQ*+*HQ*) reached a value close to 0.04. Comparing the *BQ* and *HQ* curves in Fig. 2, it can be seen that during the initial 30 min of illumination only part of *BQ* is reduced to *HQ*. More than 30% of the initial *BQ* undergoes partial oxidation and forms some intermediates, a little is fully mineralized (see TOC curve), and the rest forms a mixture with *HQ* in which the *BQ* content is about 4%. The reaction slurry contains thus a rather huge amount of unknown primary products of the *BQ* oxidation; they change the colour of the slurry to pale red. However, the red colour vanishes during further irradiation. Also, during the next 30 min the reaction of full mineralization proceeds faster. Prolonged illumination causes changes in *HQ* and *BQ* contamination similar to those observed before for the reaction of *HQ* (Fig. 1).

Figure 3 shows the variations of *HQ* and *BQ* concentrations during illumination of the equimolar slurry of hydroquinone and *p*-benzoquinone in the presence of TiO_2. Here again *BQ* partly transforms to *HQ* (the concentration of the latter increased) and partly oxidizes to other compounds. The ratio *BQ*/(*BQ*+*HQ*) lowers with time from the initial value of 0.5 to about 0.04–0.05. Upon further illumination, the changes of the concentrations of *HQ* and *BQ* follow those depicted in Figs. 1 and 2.

The products of the photocatalytic oxidation of *HQ* were extracted from the reaction mixture without and with initial acetylation and analyzed by GC-MS. Before, the hydroquinone solution was illuminated for 2 hours in the presence of titania. Only two new compounds were detected in addition to those mentioned above: 1,2,4-benzenetriol triacetate (after acetylation) and glycerol. Another reaction intermediate is presumable ethanedial as determined by HPLC. The compound was identified on the basis of its UV/Vis spectrum.

As reported in the literature, photooxidation of *HQ* and *BQ* (direct photolysis in the presence of oxygen without any photocatalyst) yields for *HQ* the dimer 2,2′,5,5′-tetrahydroxybiphenyl, for *BQ* hydroquinone, 1,2,4-benzenetriol, hydroxylated *p*-benzoquinone, and traces of 2,2′,5,5′-tetrahydroxybiphenyl [17]. Hydroxylated biphenyls were also observed in products of photocatalytic oxidation of 2,4-dichlorophenol in the presence of ZnO [19]. Other authors claim the existence of a number of aliphatic intermediates, among them acetate and formate, during photocatalytic degradation of aromatic water pollutants, including phenols, in the presence of TiO_2 [13]. The results of the present investigations are not contradictory to these reports: *BQ* yields mainly *HQ* and unidentified intermediates which decompose relatively fast during prolonged illumination in the presence of TiO_2. The photoreaction follows that observed for *HQ* (cf. Figs. 1–3). Note that the changes in *HQ* and *BQ* concentrations during photocatalytic oxidation of a 1:1

mixture of hydroquinone and *p*-benzoquinone confirm clearly the results obtained for the photocatalytic oxidation of *BQ* itself. Higher hydroxylated aromatic intermediates (1,2,4-benzenetriol), glycerol and, presumable, ethanedial were determined in the products of photocatalytic *HQ* oxidation. Acetate and formate as well as hydroxylated biphenyls may not be detected by the applied methods. However, a great amount of unidentified organic matter (see TOC curves in Figs. 1 and 2) shows that a number of aliphatic compounds and, possibly, polymers exist.

The kinetics of the photocatalytic reaction of *HQ* destruction were studied. The results, shown in Fig. 4, refer to the sum of *BQ* and *HQ*. Initial rates of the photocatalytic reaction, estimated from the data of Fig. 4, were used for further calculations. The 1/*r* *vs.* 1/*c* dependence ($r = \mathrm{d}c/\mathrm{d}t$, *i.e.* the reaction rate, *c*: concentration of the substrate) is depicted in Fig. 5. One can see from the Fig. 5 that, although the points corresponding to the initial reaction rates somewhat

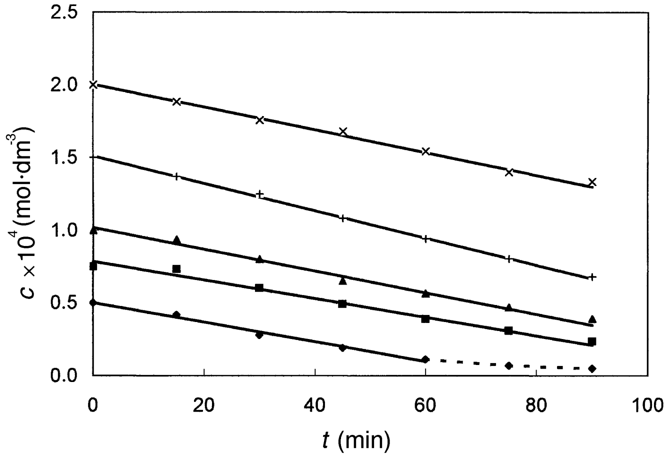

Fig. 4. Kinetics of hydroquinone disappearance; individual curves refer to different hydroquinone concentrations

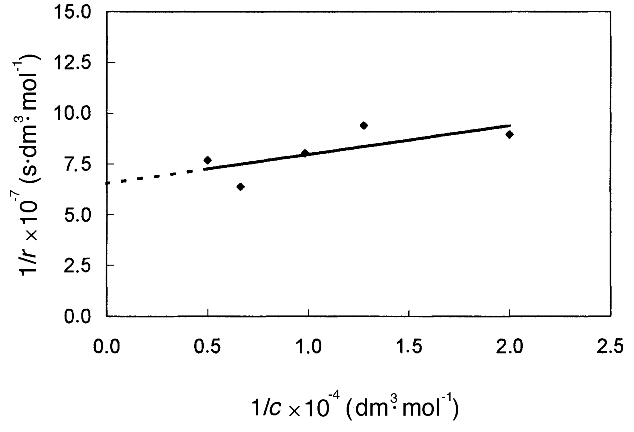

Fig. 5. Plot of 1/*r* *vs.* 1/*c* (for definition of *r* and *c*, cf. text)

scatter, a linear dependence exists rather than another kind of relationship. Therefore, the reaction shows 1st order behaviour, and the kinetic constant can be calculated [14]: $k = 1.5 \cdot 10^{-8}\,\mathrm{mol} \cdot \mathrm{dm}^{-3} \cdot \mathrm{s}^{-1}$, $K_{\mathrm{ads}} = 4.6 \cdot 10^{4}\,\mathrm{dm}^{3} \cdot \mathrm{mol}^{-1}$. First order kinetics have already been reported for the photocatalytic phenol oxidation in the presence of titania (see *e.g.* Refs [14, 20, 21] and references cited therein). The k and K_{ads} values also are close to those reported before for 1,3-benzenediol photooxidation under similar conditions [22]. The use of the initial reaction rates for kinetic calculations allows to avoid the influence of the reaction intermediates on the estimated constants. During the photocatalytic studies, illumination and oxygen content in the reactor solution were kept constant; therefore, these two variables are not included in the rate expression.

Conclusions

Photocatalytic oxidation of hydroquinone and *p*-benzoquinone – the main intermediates which are formed in the process of phenol photodestruction on illuminated titania – proceeds *via* several reaction steps which involve several reaction intermediates. Some of them were determined by HPLC and GC-MS: ethanedial, glycerol, and 1,2,4-trihydroxybenzene. Interestingly, *BQ* partly undergoes fast oxidation, partly transformation to *HQ* when irradiated in solution in the presence of TiO_2. The oxidation reaction follows that of pure *HQ*. The photocatalytic oxidation of *HQ* seems to be of 1st order *vs.* substrate concentration, in accordance with data reported in the literature for other compounds [20].

To our knowledge, this is the first study on photocatalytic oxidation of hydroquinone and *p*-benzoquinone. It is our opinion that recognition of main reaction products and rate constants of photocatalytic oxidation of dihydroxybenzenes can help to elucidate also the mechanism of the process of phenol photocatalytic destruction used in waste water treatment.

Experimental

Photocatalytic studies

The experiments were performed in a non-continuous mode (batch reactor) in a photoreactor similar to that described earlier [14, 21]. The reactor consisted of an external glass tube with a conical bottom equipped with a septum and a draft tube placed in the center of the external one. The reactor content was mixed by an air stream applied at the bottom using a needle and flowing up through the draft tube. The dimensions of the reactor were as follows: inner diameter of the external tube, 40 mm; *h*, 160 mm; inner diameter of the draft tube, 10 mm; *h*, 120 mm; total volume of the reactor, *ca.* 190 ml. The photoreactor was filled with 165 ml of a reaction solution and 0.05 g TiO_2 anatase (99.9%, Aldrich). Depending on the experiment, the reaction solution contained hydroquinone (99%, Aldrich), *p*-benzoquinone (99%, Aldrich), or a mixture (1:1) of both compounds. The titania powder was sonicated before illumination with a small volume of the reactor solution. The reactor was illuminated from a side wall with a 180 W medium pressure Hg lamp. The Pyrex walls of the reactor determined a lower limit of entering light (about 300 nm cutoff filter). The photoreactor was cooled by an air stream; the reaction temperature was maintained at 28±2°C. During the photoreaction, 1 ml of the slurry was withdrawn every 15 or 30 min using a syringe and, after filtration over Millipore Millex GV_3 units, analyzed by HPLC (Waters) using both fluorescence (Waters 474) and photodiode array (Waters 991) detectors. The reaction products were separated on a Supelcosil LC8 column using water-methanol with a gradient concentration as an eluent.

For TOC determinations, 2 ml of the irradiated slurry were withdrawn from the photoreactor every 30 min and, after filtration over the Millipore units, analyzed on a CA-10 TOC Shimadzu Analyser.

GC-MS experiments were performed as follows: firstly, 165 ml $2 \cdot 10^{-4}$ *M HQ* and 0.05 g TiO_2 were illuminated 2 h in the photoreactor; next, the phenols in the slurry were acetylated according to a procedure described in Refs. [22, 23]. After extraction with CH_2Cl_2 and partial evaporation of the extractant, the residue was analyzed on a mass spectrometer AMD-402 (Germany) coupled with a gas chromatograph (Hewlett Packard Model 5890 Series II). The analyzed products were separated on a DB-1 column using a temperature program (80–300°C). For MS analysis, an ionization energy of 70 eV and an acceleration voltage of 8 kV were applied. Simple extraction of the reaction products (without acetylation) from the slurry after illumination was also performed, and products were analyzed by GC-MS.

The photocatalyst

The titania – TiO_2 anatase, 99.9%, Aldrich – possessed a BET specific surface area of $9.85\,m^2 \cdot g^{-1}$ as measured on a Micromeritics ASAP 2010 apparatus. It showed the typical anatase absorption spectrum with an absorption onset at about 400 nm. The reflectance spectrum, not shown in this paper, was measured on Specord M-40 spectrophotometer. The water used for the photocatalytic studies was doubly distilled in a quarz water still. All reactants were of *p.a.* purity or HPLC specified.

Acknowledgements

The authors are grateful to the Commitee of Scientific Research (KBN) in Warsaw, Poland (project 6 P04G 055 12) for funds to perform this work. The authors thank Mrs. *Danuta Siatkowska* from the A. Mickiewicz University in Poznań, Poland, for GC-MS analyses.

References

[1] Anpo M (1989) Res Chem Intermed **11**: 67
[2] Gerischer H, Heller A (1991) J Phys Chem **95**: 5261
[3] Brezova V, Stasko A, Lapcik Jr L (1991) J Photochem Photobiol A Chem **59**: 115
[4] Brezova V, Stasko A (1994) J Catal **147**: 156
[5] Lawless D, Serpone N, Meisel D (1991) J Phys Chem **95**: 5166
[6] Goldstein S, Czapski G, Rabani J (1994) J Phys Chem **98**: 6586
[7] Fox MA (1993) The Role of Hydroxyl Radicals in the Photocatalysed Detoxification of Organic Pollutants: Pulse Radiolysis and Time Resolved Reflectance Measurements. In: Ollis DF, Al-Ekabi H (eds) Photocatalytic Purification and Treatment of Water and Air. Elsevier, Amsterdam p 163
[8] Drapper RB, Fox MA (1990) Langmuir **6**: 1396
[9] Stafford U, Gray KA, Kamat PV (1994) J Phys Chem **98**: 6343
[10] Cermenati L, Pichat P, Guillard C, Albini A (1997) J Phys Chem B **101**: 2650
[11] Kesselman JM, Weres O, Lewis NS, Hoffmann MR (1997) J Phys Chem B **101**: 2637
[12] Okamoto K, Yamamoto Y, Tanaka H, Itaya A (1985) Bull Chem Soc Jpn **58**: 2015
[13] Pichat P, Guillard C, Maillard C, Amalric L, D'Oliveira JC (1993) TiO_2 Photocatalytic Destruction of Water Pollutants: Intermediates; Properties – Degradability Correlation; Effects of Inorganic Ions and TiO_2 Surface Area; Comparisons with H_2O_2 Processes. In: Ollis DF, Al-

Ekabi H (eds) Photocatalytic Purification and Treatment of Water and Air. Elsevier, Amsterdam p 207
[14] Sobczyński A, Gimenez J, Cervera-March S (1997) Monatsh Chem **128**: 1109
[15] Sobczyński A, Duczmal Ł (to be published elsewhere)
[16] Stoddart JF (ed) (1979) Comprehensive Organic Chemistry, vol 1. Pergamon Press, Oxford, p 739
[17] Joshek HJ, Miller SJ (1966) J Am Chem Soc **88**: 3273
[18] Fuson FC (1966) Reactions of Organic Compounds. Wiley, New York
[19] Sehili T, Boule P, Lemaire J (1991) Chemosphere **22**: 1053
[20] Turchi CS, Ollis DF (1990) J Catal **122**: 202
[21] Sobczyński A, Gimenez J, Cervera-March S (1996) Pol J Appl Chem **40**: 103
[22] Duczmal Ł, Sobczyński A (1998) React Kinet Catal Lett (submitted)
[23] Standard Methods for the Examination of Water and Wastewater (1992) 18th edn, American Public Health Association, p 6–77
[24] Bao ML, Pantani F, Barbieri K, Burrini D, Griffini O (1996) Chromatographia **42**: 227

Received August 3, 1998. Accepted (revised) September 15, 1998