Phenol destruction by photocatalysis on TiO$_2$: an attempt to solve the reaction mechanism

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Abstract

Six hydroxylated aromatic compounds, *p*-benzoquinone and four aliphatic compounds were detected as intermediates of the reaction of phenol photocatalytic oxidation in the presence of illuminated TiO$_2$. The concentration of catechol, hydroquinone and *p*-benzoquinone was determined quantitatively along with that of phenol in the course of the photoreaction. The reactions of TiO$_2$-photooxidation of phenol and its primary intermediates—dihydroxybenzenes show 1st order behaviour. The use of initial reaction rates for kinetic studies is recommended because of many competitive reactions in illuminated suspensions of titanium dioxide. A possible mechanism of phenol full mineralisation is presented.
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1. Introduction

Extensive studies on photocatalysis on semiconductors, in particular on illuminated surface of titanium dioxide, were commenced over 25 years ago. Although the interest was focused firstly on hydrogen photoevolution from water or organic wastes, some papers were published which concerned oxidation of organic compounds dissolved in water. In the first period, the properties of semiconductors were thoroughly investigated and described, including semiconductor modifications and sensitisation, and improvement of hydrogen evolution ability, see, e.g. [1–10]. However, even in the early stage of development of the new branch of chemistry the interest was focused on the reactions which occurred inside illuminated suspensions of semiconductors such as titania. For example, the formation of •OH radicals was observed in aqueous TiO$_2$ suspensions and their role was explained by Bard and co-workers [11,12]. The participation of the radicals in the reactions of photocatalytic oxidation of organic compounds has been then studied by many authors [13–18]. The application of the processes of TiO$_2$-photocatalysis to water decontamination has been also postulated [14,19–24]. Since over 15 years, the stud-

ies on photocatalytic degradation/mineralisation of water organic pollutants have been undertaken in many laboratories all over the world, see, e.g. review papers [25–27] and references therein.

Kinetics of the photooxidation of organic water impurities on illuminated titania surface, including phenol and its derivatives, has been generally regarded to be based on a Langmuir–Hinshelwood equation and first order of the reaction kinetics versus initial substrate concentration was established univocally by many authors, see, e.g. [28–32]. Also, phenol adsorption isotherm on TiO$_2$ was investigated and adsorption equilibrium constant calculated both from adsorption and reaction kinetics studies [33]. The role of oxygen in the photooxidation of organic molecules on semiconductor particles has been explained [34,35] and some modifications of the semiconductor surface have been proposed in order to enhance O$_2$ reduction by photogenerated electrons [36–40].

Full mineralisation of organic compounds, also phenols and other aromatics, on the surface of illuminated titania proceeds via many steps, which make one-electron oxidation or reduction reactions. A full set of the reactions which take place (or are likely) on illuminated semiconductors has been given by Gerischer and Heller [34]. Under illumination, organic molecules react with photogenerated holes or, more probably, with photoinduced •OH radicals, giving in result a number of hydroxylated reaction intermediates. Determination of the compounds was a subject of many inves-

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tigations [41–47]. However, until now a full mechanism of photooxidation of phenol and its derivatives has not been established.

The present paper represents an approach to elucidate, at least in part, the mechanism of phenol photocatalytic destruction by studying qualitatively and, in some cases, quantitatively, intermediates of phenol and dihydroxybenzenes photooxidation. Also, the kinetics of phenol and the dihydroxy derivatives was studied and k and K_{ads} values were calculated from the Langmuir–Hinshelwood equation.

2. Experimental

Photocatalytic experiments were carried out in an air lift loop reactor similar to the one described before [33,40]. The reactor content was mixed by an air stream ($3\,dm^3\,h^{-1}$) controlled by a draft tube. A non-continuous mode of the process was applied (batch reactor). During the experiment, the photoreactor contained $165\,cm^3$ of phenol solution and $0.05\,g$ of TiO_2 anatase, 99.9%, Aldrich. Depending on the experiment, the concentration of the phenol (Aldrich, 98%) was 0.5, 0.75, 1.0, 1.5 or $2.0 \times 10^{-4}\,mol\,dm^{-3}$. The TiO_2 powder was sonicated before illumination with a small amount of the phenol solution for 5 min. The reactor was illuminated from side with a light of a 180 W medium pressure mercury lamp. The incident light flux was $0.156\,\mu mol$ quanta/s, as measured by uranyl-oxalic actinometry [48]. The Pyrex walls of the photoreactor determined lower limit of entering light (about 300 nm cutoff filter). The photoreactor was cooled by a stream of air; the reaction temperature was maintained at $28 \pm 2\,°C$. During the photoreaction $1\,cm^3$ of the slurry was withdrawn every 15 min or 30 min using a syringe and, after filtration over Millipore Millex GV_3 units, analysed by HPLC (Waters) using both fluorescence (Waters 474) and photodiode array (Waters 991) detectors. The detectors were coupled together. The reaction products were separated on a Supelcosil LC8 column using water–methanol with a gradient concentration as an eluent. For TOC determinations $2\,cm^3$ of the irradiated slurry was withdrawn from the photoreactor every 30 min and, after filtration over the Millipore filter, analysed on a TOC Shimadzu analyser.

GC–MS measurements were performed as follows. Primarily, $165\,cm^3$ $2 \times 10^{-4}\,mol\,dm^{-3}$ phenol and $0.05\,g$ TiO_2 were illuminated 2 h in the photoreactor (see above). Next, the phenols in the slurry were acetylated using the procedure described in the literature [49,50]. Then, after extraction with methylene chloride and partial evaporation of the extractant, the residue was analysed on the mass spectrometer AMD-402 (Germany) coupled with the gas chromatograph, Hewlett-Packard model 5890 series II. The analysed products were separated on the DB-1 column using programmed temperature 80–300 °C. For MS analysis, the ionisation energy 70 eV and accelerated voltage 8 kV were applied. Sim-

ple extraction of the reaction products (without acetylation) from the slurry after illumination was also done and products were analysed by GC–MS.

The titania–TiO_2 anatase, 99.9%, Aldrich, had a specific surface area $9.85\,m^2\,g^{-1}$ as measured on a Micromeritics ASAP 2010 apparatus. It showed also typical anatase absorption spectrum with an absorption onset at about 400 nm. The reflectance spectrum—not shown in the paper—was measured on a Specord M-40 spectrophotometer.

The water used for the photocatalytic studies was doubly distilled in a quartz water still. All reactants were of p.a. purity or HPLC-specified ones.

3. Results and discussion

Illumination of phenol (and dihydroxybenzenes, see below) in the presence of titanium dioxide was conducted in a specially designed three phase fluidised bed reactor using an air lift controlled by a draft tube. The reactor design and its advantages have been described previously, see, e.g. [33,40]. It can be added here that, besides providing bulk circulation of gas, liquid and solid, the reactor assures high gas (air) holdup and high contact efficiencies between the three phases. Therefore, it is a good tool also for measurements of kinetic factors of the conducted reaction or photoreaction.

It was observed before in our studies that the rate of phenol destruction in the presence of illuminated titania increased with increasing substrate concentration in the range 2×10^{-4} to $6 \times 10^{-4}\,mol\,dm^{-3}$ and was strongly retarded at 1.0×10^{-3} and $1.6 \times 10^{-3}\,mol\,dm^{-3}$. The reasons for the observed phenomenon have been also discussed [40]. Therefore, in this studies, which aim was to elucidate a possible mechanism of phenol photooxidation in the presence of titania, its concentration as low as $2 \times 10^{-4}\,mol\,dm^{-3}$ was used. Also kinetic measurements of the process were conducted using phenol concentration in the range of 0.5×10^{-4} to $2.0 \times 10^{-4}\,mol\,dm^{-3}$.

The amount of titanium dioxide, 0.5 g, used in these studies, was well-chosen experimentally. Raising the photocatalyst amount up to about 0.02 g (per 165 ml of the solution in the reactor) the photoreaction rate increased. Above that value, the rate was constant owing to light scattering on TiO_2 particles (which increases with concentration of the solid) [40]. Therefore, in order to omit any influence of the concentration of titania, 0.05 g of the semiconductor powder was used in all studies. Similarly, a threshold value was found for airflow rate; the rate of $100\,cm^3\,min^{-1}$ was chosen experimentally as an optimum one. It was also confirmed in black experiments that neither 3-h air flushing nor illumination of phenol solution with no titania additives caused any noticeable changes in the phenol concentration measured by HPLC [40].

Fig. 1 shows results of HPLC and TOC measurements of the reaction products of phenol destruction on illuminated TiO_2. Some conclusions arise from the results shown

in the figure. After 3 h of illumination, a little more than 25% of the initial phenol was totally mineralised (i.e. to CO_2 and H_2O; see TOC curve). During that time the disappearance of phenol itself was much faster: more than 65% of the substrate was photocatalytically oxidised on the illuminated semiconductor. Hydroquinone, p-benzoquinone and catechol were detected and determined quantitatively as main reaction intermediates. Having in mind that the photocatalytic oxidation of organic compounds on illuminated TiO_2 proceeds via $^\bullet OH$ attack on the substrate, dihydroxybenzenes are the primary products of the process. The compounds, and also 1,3-dihydroxybenzene (resorcinol), were detected by other authors; see Section 1. However, in this study the concentration of 1,2- and 1,4-hydroxybenzenes, and of p-benzoquinone, was monitored quantitatively in the course of the photocatalytic reaction. It should be added here that also 1,3-dihydroxybenzene was detected in the reaction products by GC–MS, see below, although in the amount not detectable quantitatively. After 3-h illumination, the amount of hydroquinone was 14.7%, that of catechol 4.1% and p-benzoquinone 2.4%. The sum of the three compounds amounts to 21%, assuming 100% for initial phenol concentration. However, the difference between phenol and TOC curve in Fig. 1 shows that about 38% of organic matter still exist in the reaction slurry after 3-h illumination. Therefore, about 17% of initial phenol were converted into other intermediates than the three ones mentioned above.

As it was mentioned in the Section 1, kinetics of photooxidation of organic water impurities on illuminated titanium dioxide is generally regarded to be based on a Langmuir–Hinshelwood equation. Okamoto et al. [32] proposed a kinetic expression, which included initial substrate concentration, amount of semiconductor powder, oxygen partial pressure and intensity of incident light. In this study phenol concentration is the only variable, the other three factors remain constant in all experiments. Therefore, assuming the Langmuir–Hinshelwood model for the photocatalytic reaction, the rate equation is as follows:

$$r = -\frac{dc}{dt} = \frac{kKc}{1 + Kc} \tag{1}$$

where c is the substrate concentration in water, k a rate constant, and K a constant of adsorption equilibrium.

For 1st order reaction kinetics, the dependence of $1/r$ on $1/c$ should be linear.

Kinetics of the photocatalytic reaction of phenol destruction was studied using five different concentration of the substrate: 0.5, 0.75, 1.0, 1.5 and 2.0×10^{-4} mol dm^{-3}. Fig. 2 shows variations of phenol concentration during illumination. The presented c versus t curves were the basis for calculations of initial reaction rates. Note, that the large content of various organic intermediates and their competitive reactions with TiO_2-photogenerated $^\bullet OH$ radicals required the use of the initial photoreaction rates for kinetic calculations of the photocatalytic oxidation of phenol. Basing on thus calculated rates, a graph of $1/r$ (s dm^3 mol^{-1}) versus $1/c$ (dm^3 mol^{-1}) was drawn, see Fig. 3, where r is the reaction rate dc/dt and c is the initial concentration of the phenol solution. One can see from Fig. 3 that although the points corresponding to the initial reaction rates somewhat scatter, a linear dependence with a correlation factor $R^2 = 0.94$ exists rather than another kind of the relationship. Therefore, the reaction shows 1st order behaviour and kinetic constants, k and K, can be easy calculated from the mentioned Langmuir–Hinshelwood equation. Their values are depicted in Table 1.

Recently, some papers have been published from this laboratory on kinetics and intermediates of catechol, resorcinol and hydroquinone decomposition on illuminated TiO_2 [51–53]. For the all three compounds, 1st order reaction
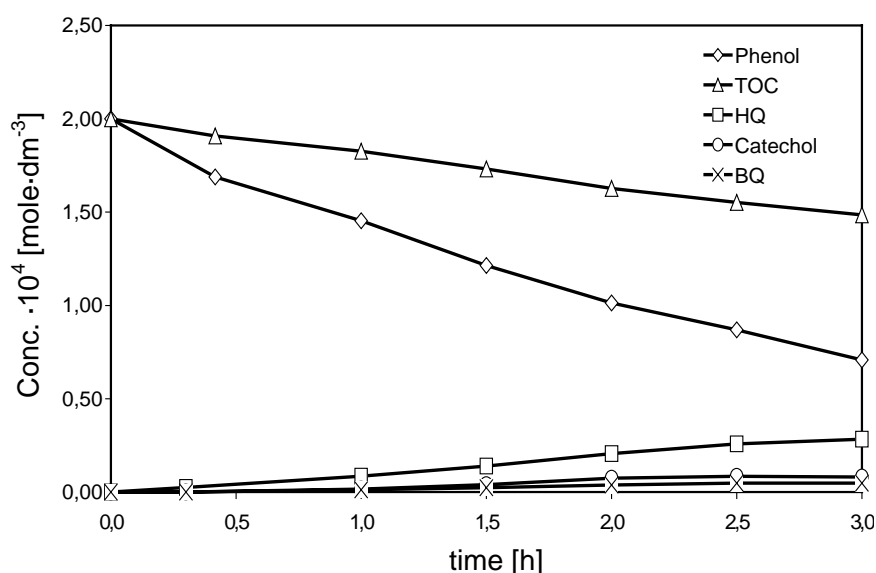

Fig. 1. The results of HPLC and TOC analysis of the products of phenol photodecomposition on titania.
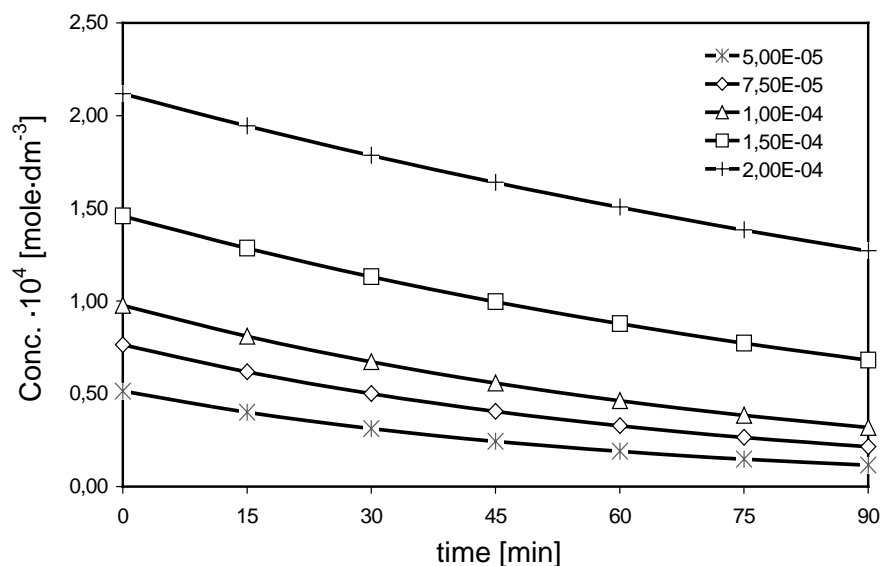
Fig. 2. Kinetic curves of phenol decay. Individual curves refer to different phenol concentration.
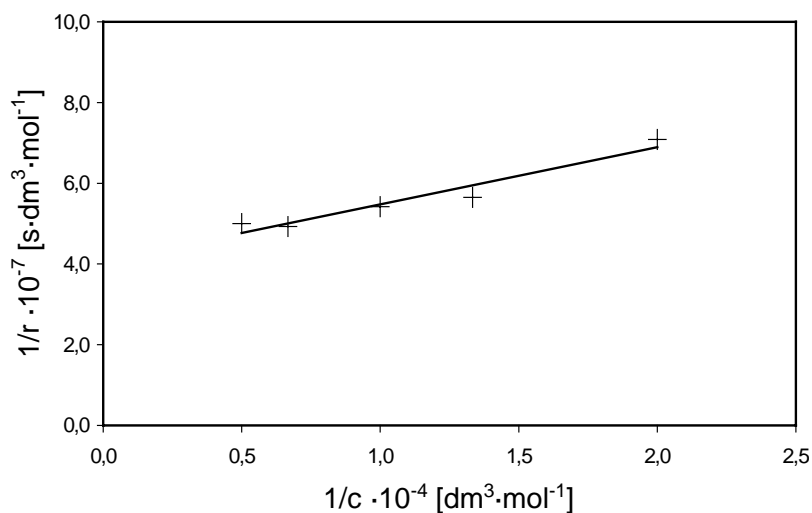

Fig. 3. Plot of $1/r$ vs. $1/c$.

kinetics was found. Also, k and K were calculated from the Langmuir–Hinshelwood equation. The values are depicted in Table 1 together with these for phenol decomposition.

The photoreactions of the all four compounds (Table 1) show 1st order behaviour. Therefore, reactions of photocatalytic oxidation of the three intermediate compounds, 1,2-, 1,3- and 1,4-dihydroxybenzenes are competitive to phenol oxidation. The rate of decomposition of each compound depends on its concentration in the solution and on the rate constant, k. The concentrations of catechol and hydroquinone (the case of benzoquinone is discussed below) increase at the beginning of illumination, then the changes are smaller. The slow changes of the concentrations are on account of simultaneous formation (from phenol) and decomposition of the compounds. Much faster disappearance of phenol itself is caused both by its high concentration and the highest

k value; see Fig. 1 and Table 1. According to the substitution rules $^{\bullet}$OH radicals attack the phenol molecule with higher probability in 2 and 4 position versus OH group of the aromatic ring. Therefore, it is not surprising, that only traces of resorcinol were observed in the reaction mixture.

Table 1
Reaction rate constants (k) and constants of adsorption equilibrium (K_{ads}) for phenol and dihydroxybenzenes

	k[a] (mol dm^{-3} s^{-1})	K_{ads}[b] (dm^3 mol^{-1})
Phenol	2.46×10^{-8}	2.86×10^4
Catechol	2.03×10^{-8}	1.63×10^4
Resorcinol	2.09×10^{-8}	3.18×10^4
Hydroquinone	1.31×10^{-8}	1.90×10^4

[a] Standard deviation: 0.42×10^{-8}.
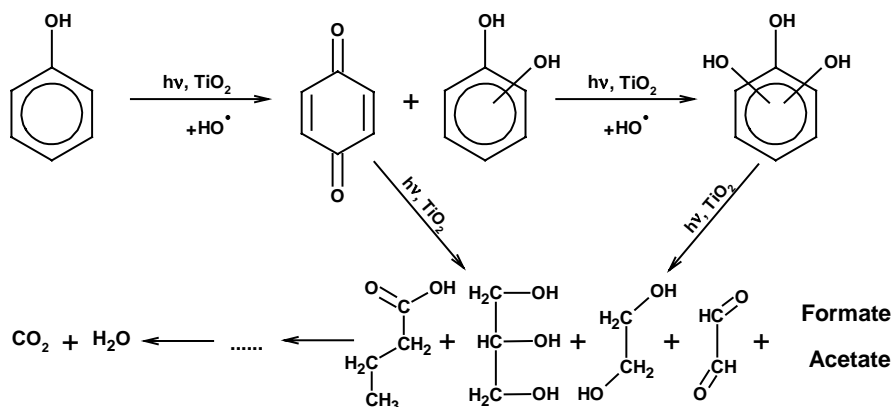[b] Standard deviation: 0.65×10^4.

Fig. 4. A possible mechanism of phenol destruction on illuminated TiO_2.

The higher amount of hydroquinone (if compare to catechol) is on account of much lower reaction rate constant for this compound.

The results of GC–MS studies of the photocatalytic reaction products of phenol, catechol, resorcinol and hydroquinone extracted with methylene chloride are shown in Table 2. The extractions were performed for the reaction mixtures taken directly from the photoreactor and after acetylation. The results of the GC–MS studies of the reaction intermediates of photocatalytic oxidation of the dihydroxybenzenes have been already published [51–53]. Using the higher concentration of the compounds, the products of their photooxidation could be detected more precisely. Certainly, these products are also the intermediates of the photocatalytic oxidation of phenol itself.

Basing on the obtained results, a probable mechanism of phenol oxidation in the presence of illuminated titanium dioxide can be depicted, see Fig. 4.

Unfortunately, we are aware, that the mechanism shown in Fig. 4 is very incomplete. Moreover, some remarks regarding the mechanism should be done here in the light of the present and former our studies [39,40,51–53]. It has been shown in one of the recent paper [52] that hydroquinone and p-benzoquinone exist in equilibrium in an aerated solution, also in the presence of illuminated TiO_2. Therefore,

p-benzoquinone can be formed in three different ways: (1) by •OH attack on hydroquinone molecule, (2) in the reaction of that molecule with holes photogenerated in titanium dioxide; and (3) by direct oxidation of hydroquinone by oxygen dissolved in water. Moreover, hydroquinone can be hydrated further (see Table 2) and it is not certain, if oxidative opening of an aromatic ring proceeds solely via benzoquinone oxidation. However, it was shown before [52] that 40% of 2×10^{-4} m p-benzoquinone solution underwent fast oxidation (in 15 min) in the presence of illuminated TiO_2. Also, under the conditions, about 60% of the compound were transferred into hydroquinone. Therefore, further oxidation of p-benzoquinone can lead directly to oxygen-contained aliphatic compounds with no further hydroxylation of the compound, via the route shown in Fig. 4. Catechol, similarly to hydroquinone, forms o-benzoquinone. The compound is, however, very unstable and hence its absence in the detected products of photochemical oxidation of phenol or catechol.

There exist probably a variety of aliphatic intermediates in the reaction mixture. Only four of the compounds were detected in this study; formic and acetic acids were inserted into the reaction mechanism (Fig. 4) basing on literature [41]. It is also possible that some polymeric compounds are formed, including biphenols, especially at higher phenol concentration [43]. The formation of these compounds, which are insoluble in water and probably stick on the surface of titania, can be the reason of the observed retardation of the photoreaction at higher phenol concentration.

4. Conclusions

Phenol and its dihydroxy derivatives undergo destruction in the presence of illuminated TiO_2 according to 1st order kinetics. Hence, in a mixture their reactions are competitive. It is therefore proposed that initial reaction rates should be taken into account for reaction kinetic studies. p-benzoquinone, six hydroxylated aromatics and four aliphatic compounds have been found to be intermediates of phenol full photocatalytic mineralisation. Three of

Table 2
GC–MS studies of the products of TiO_2-photocatalytic destruction of phenol and dihydroxybenzenes

	Direct extraction	Extraction after acetylation
Phenol	Resorcinol	Catechol
	Hydroquinone	Hydroquinone
Catechol		Glycol
		1,2,4-Benzenetriol
Resorcinol	Butanoic acid anhydride	1,2,4-Benzenetriol
		1,3,5-Benzenetriol
Hydroquinone	Glycerin	1,2,4-Benzenetriol
	Ethanedial	

them—catechol, hydroquinone and *p*-benzoquinone—have been determined quantitatively and the changes of their concentrations have been recorded during the reaction. Basing on the results of phenol, dihydroxybenzenes and *p*-benzoquinone reactions a possible mechanism of phenol photocatalytic destruction has been proposed. It is also postulated that for disclosure of the full reaction mechanism careful studies should be undertaken on TiO_2-photocatalytic oxidation of various intermediate compounds of the phenol destruction on illuminated titania.

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