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Spin Trap Study of Hydroxyl Radicals Formed in the Photocatalytic System TiO_2–Water–*p*-Cresol–Oxygen

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The formation of hydroxyl radicals in the photocatalytic system TiO_2–water–*p*-cresol–oxygen employing 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as a spin trap was investigated at various initial concentrations of *p*-cresol. The reciprocal values of the relative concentrations of the DMPO adduct with hydroxyl radicals (DMPO-OH$^\bullet$) exhibited a linear dependence upon the initial concentrations of *p*-cresol. The data obtained are well described by the Langmuir–Hinshelwood kinetic model. The adsorption isotherms, separately determined for DMPO and *p*-cresol on TiO_2, indicated that the adsorption of DMPO is three times higher than that of *p*-cresol. The adsorption measured at constant *p*-cresol concentrations and variable DMPO concentrations confirms a competitive adsorption and implies that both species adsorb on the same TiO_2 sites. © 1994 Academic Press, Inc.

INTRODUCTION

Photocatalytic reactions on semiconductor powders have attracted a remarkable amount of attention (1). The research has been focused primarily on water cleavage (2–4), organic synthesis (5–7), and purification of waste water from inorganic (8–10) and organic (11–14) compounds. Considerable attention has recently been focused on the mechanisms and kinetics of photocatalytic degradation of aromatic compounds in aqueous titanium dioxide suspensions (15–23) and on the role of hydroxyl radicals in these processes (24–25). EPR investigations confirmed the formation of high concentrations of hydroxyl radicals in the irradiated aqueous TiO_2 suspensions in the presence of oxygen (26–28).

The photocatalyzed mineralization of cresols in aqueous titanium dioxide suspensions was studied by Terzian *et al.* (22) and major hydroxylated intermediates 4-methylcatechol and methylhydroquinone were identified. The influence of *p*-cresol concentration, in the presence of oxygen and hydrogen peroxide, on the photodegradation rate of *p*-cresol in aqueous TiO_2 suspensions was also studied in our laboratory (29). The hydroxylated intermediate (4-methylcatechol) and the products of methyl group oxidation (4-hydroxybenzaldehyde and 4-hydroxybenzoic acid) were found.

The aim of this study was to find a suitable kinetic description for the formation of hydroxyl radicals in the aqueous titanium dioxide suspensions in the presence of *p*-cresol employing spin trap techniques.

EXPERIMENTAL

Titanium dioxide P25 from Degussa (Germany) was used in all experiments; the concentration of TiO_2 in the suspensions, $[TiO_2]$, was 1 g dm^{-3}. Degussa P25 is an active photocatalyst (28, 30) with surface area of 50 ± 5 $m^2\ g^{-1}$, existing predominantly in the anatase form (80% anatase, 20% rutile) (18) and containing small amounts of SiO_2 and Al_2O_3 (28).

UV–visible spectra were measured on a Philips spectrophotometer PU 8800 (U.K.). The suspensions were centrifuged 30 min at 5000g on a centrifuge MLW T62.2 (Germany) before measuring the UV spectra.

EPR spectra were recorded at a temperature of 293 K on a Bruker SCR 200E spectrometer coupled with an Aspect 2000 computer (Germany). The cavity was continuously flushed with argon at 293 K to eliminate overheating of the sample by irradiation. The temperature increase during irradiation was less than 2°C. 5,5-Dimethyl-1-pyrroline-*N*-oxide from Sigma Chemicals, freshly distilled before use and kept under an argon atmosphere at -25°C, was applied as a spin trap. In all EPR experiments, the initial DMPO concentration in the suspensions was constant ($[\mathrm{DMPO}]_0 = 0.01$ mol dm^{-3}).

A 500-W high-pressure mercury lamp (Narva, Germany) emitting predominantly light with a wavelength of 365 nm was used without any filter for irradiation of the suspension. In experiments employing a Pyrex filter ($\lambda >$ 300 nm), the same results were obtained as in those without filters, but slightly lower EPR signal intensities were observed. Para-cresol (Lachema, Czech Republic) was recrystallized before use. All aqueous solutions and suspensions were prepared using redistilled water.

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The aqueous suspension of TiO_2, p-cresol, and DMPO was bubbled for 5 min with oxygen at 293 K under strictly the same conditions, then immediately placed into the quartz cell for measurements.

Two types of experiments were carried out:

(i) interrupted irradiation; i.e., the sample with the chosen p-cresol concentration was irradiated for a time t_{ir}; then the EPR spectrum was recorded and this was repeated with an increased t_{ir} time (Fig. 1). A similar procedure was performed with the samples at various initial p-cresol concentrations (Fig. 2).

(ii) continuous irradiation; i.e., the EPR spectrometer was tuned to the position of maximum intensity of the second line of DMPO–OH$^\cdot$; then the irradiation was started and the change in the EPR signal intensity, I_{EPR}^{rel}, was recorded with time (Fig. 3). The position of the second line was checked, comparing it with the resonance of an external marker.

To elucidate the contribution of the noncatalytic reactions to the formation of $^\cdot$OH radicals, blank experiments, i.e., photolysis in the presence of various p-cresol concentrations and the absence of TiO_2 at various irradiation times, was carried out. Under these conditions, the yield of $^\cdot$OH radicals was about two magnitudes lower than in TiO_2 suspensions and consequently can be neglected in the evaluation of the photocatalytic reaction.

The concentrations of p-cresol and DMPO adsorbed on the titanium dioxide surface at a temperature of 295 K were measured by means of UV spectroscopy. The titanium dioxide was removed from the systems by centrifuge

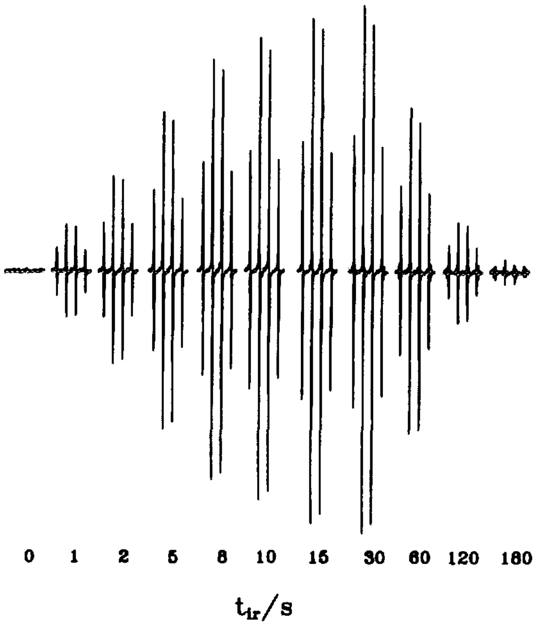


FIG. 1. EPR spectra of DMPO–OH$^\cdot$ recorded in the sample after various irradiation times t_{ir}; $[TiO_2]$ = 1 g dm^{-3}, $[DMPO]_0$ = 0.01 mol dm^{-3}, $[CR]_0$ = 0.01 mol dm^{-3}.

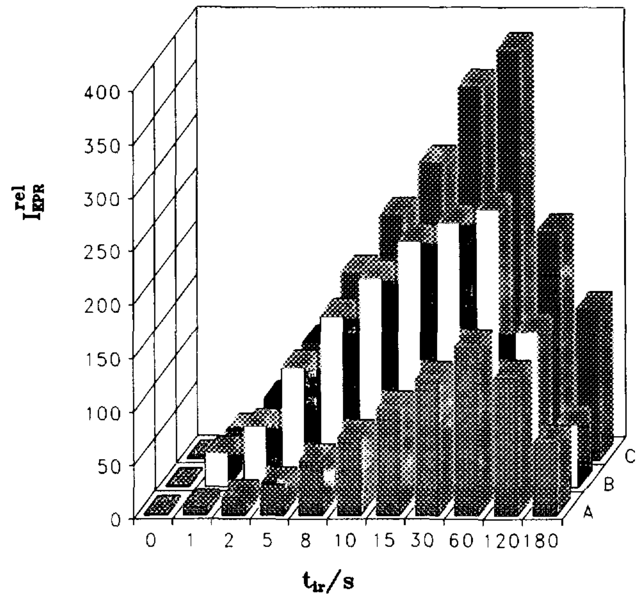


FIG. 2. Relative intensity of the EPR signal of DMPO–OH$^\cdot$ after various irradiation times t_{ir} at various initial concentrations of p-cresol; $[TiO_2]$ = 1 g dm^{-3}, $[DMPO]^0$ = 0.01 mol dm^{-3}, (A): $[CR]_0$ = 1 × 10^{-3} mol dm^{-3}, (B): $[CR]_0$ = 6.6 × 10^{-4} mol dm^{-3}, (C): $[CR]_0$ = 3.3 × 10^{-4} mol dm^{-3}.

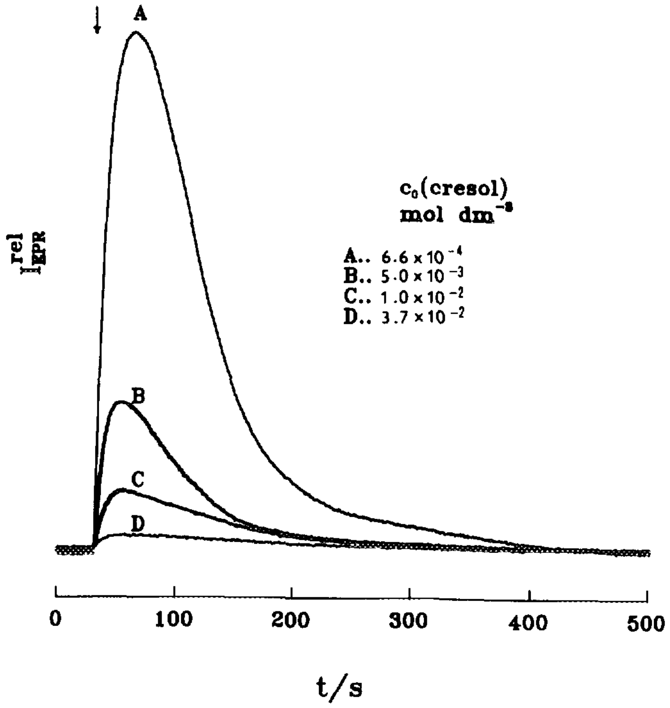


FIG. 3. Dependence of the relative intensity of the EPR signal of DMPO–OH$^\cdot$ on the irradiation time in the photocatalytic systems at various initial p-cresol concentrations (arrow indicates start of irradiation).

6h after preparing the suspensions, and the extent of adsorption was determined from the calibration curves. To prevent the photocatalytic processes during the adsorption measurements, all vessels used were covered with aluminum foil and all operations with suspensions were carried out in a dark room under red light.

Kinetic Evaluation

The formation of reactive intermediates in the irradiated aqueous suspension of titanium dioxide in the presence of oxygen may be described by the following equations (26):

$$TiO_2 + h\nu \xrightarrow{h\nu > E_{bg}} TiO_2(h^+ + e^-) \qquad [1]$$

$$O_2 + e^- \rightarrow (O_2^-)_s \qquad [2]$$

$$OH^- + h^+ \rightarrow {}^{\cdot}OH \qquad [3]$$

$${}^{\cdot}OH + \text{surface/ads. compounds} \rightarrow \text{oxidation products}, \qquad [4]$$

where h^+ is a photogenerated hole, e^- is a photogenerated electron, E_{bg} is the band gap energy of TiO_2, and the surface state is labelled by the subscript s.

Two different types of adsorption centers are assumed to exist on the TiO_2 surface (15, 23):

(i) Ti^{III} sites (adsorption of the oxygen), and

(ii) Ti^{IV}–OH^- sites (adsorption of the organic reactant).

Kinetic studies of the photocatalytic degradation of organic compounds showed that the rate of the organic substrate removal may be expressed by means of the Langmuir—Hinshelwood kinetic model (11, 15, 17, 23, 24, 31, 32):

$$r = k\,\Theta_{O_2}\Theta_S, \qquad [5]$$

where r is the conversion rate of the organic compound, k is the rate constant, Θ_{O_2} is the surface fraction of TiO_2 covered by oxygen, and Θ_S is the surface fraction of TiO_2 covered by the organic reactant, referred to henceforth as the substrate.

As the adsorbed oxygen acts as an electron acceptor hindering the electron–hole recombination, the hydroxyl radical concentration depends on the fractional sites coverage by oxygen, Θ_{O_2}, which may be described by the Langmuir adsorption isotherm (15, 32):

$$\Theta_{O_2} = \frac{K_{O_2}[O_2]}{1 + K_{O_2}[O_2]}, \qquad [6]$$

where K_{O_2} is the equilibrium adsorption constant of oxygen, and $[O_2]$ is the oxygen concentration.

Under the experimental conditions used in our set of experiments, a constant light flux and a constant surface concentration of oxygen, $\Theta_{O_2}^{eq}$, reaching the equilibrated value at a temperature of 293 K for the short irradiation times, can be assumed. Equation [5] may be simplified into the form

$$r = k_{exp}\,\Theta_S, \qquad [7]$$

where

$$k_{exp} = k\,\Theta_{O_2}^{eq}. \qquad [8]$$

The surface fraction of TiO_2 covered by organic substrate S, Θ_S, may be expressed similarly (15):

$$\Theta_S = \frac{K_S[S]}{1 + K_S[S] + \sum_i K_i[I_i]}, \qquad [9]$$

where K_S and K_i are the equilibrium adsorption constants of the organic substrate S and intermediates I_i, respectively, formed during the photocatalytic degradation of substrate, [S] is the concentration of the organic substrate at time t, and $[I_i]$ are the concentrations of the intermediates at the same time.

Under the assumptions (15, 31) that

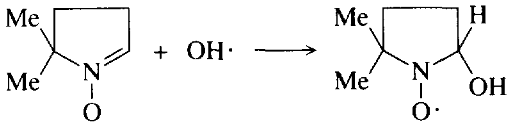
$$[S] + \sum_i [I_i] = [S]_0 \qquad [10]$$

$$K_S[S] + \sum_i K_i[I_i] = K_S[S]_0, \qquad [11]$$

where $[S]_0$ is the initial concentration of the substrate, Eq. [7] can be rewritten as

$$r = k_{exp}\frac{K_S[S]}{1 + K_S[S]_0}. \qquad [12]$$

If DMPO is present in the photocatalytic system, hydroxyl radicals are trapped according to Eq. [13] and the concentration of DMPO–OH· can be followed by means of EPR (33).



DMPO DMPO–OH· [13]

Applying Eq. [12] for DMPO substrate, the following equation may be written:

$$r^0 = -\frac{d[\text{DMPO}]}{dt} = \frac{d[\text{DMPO–OH}^{\cdot}]}{dt} = k_{exp}\frac{K_{\text{DMPO}}[\text{DMPO}]}{1 + K_{\text{DMPO}}[\text{DMPO}]_0}, \qquad [14]$$

where K_{DMPO} is the equilibrium adsorption constant of

DMPO, [DMPO] is the concentration of DMPO at time t, [DMPO–OH$^\cdot$] is the concentration of the spin adduct at the same time t, and $[\mathrm{DMPO}]_0$ is the initial concentration of DMPO, i.e., $[\mathrm{DMPO}]_0 = [\mathrm{DMPO}] + [\mathrm{DMPO{-}OH}^\cdot]$.

If, additionally, p-cresol is present in the photocatalytic system, a competitive adsorption and consequently also a competitive photocatalytic reaction occurs between DMPO and p-cresol on the active surface centers; i.e., p-cresol acts as an inhibitor in the DMPO–OH$^\cdot$ formation. Then, using similar formalism as in Eq. [14], the rate, r, for DMPO–OH$^\cdot$ formation accounting for the competitive adsorption is described by

$$r = -\frac{d[\mathrm{DMPO}]}{dt} = \frac{d[\mathrm{DMPO{-}OH}^\cdot]}{dt} = k_{\mathrm{exp}}\frac{K_{\mathrm{DMPO}}[\mathrm{DMPO}]}{1 + K_{\mathrm{DMPO}}[\mathrm{DMPO}]_0 + K_{\mathrm{CR}}[\mathrm{CR}]_0}. \quad [15]$$

The quotient of both rates (r^0/r) is given by

$$\frac{r^0}{r} = \frac{1 + K_{\mathrm{DMPO}}[\mathrm{DMPO}]_0 + K_{\mathrm{CR}}[\mathrm{CR}]_0}{1 + K_{\mathrm{DMPO}}[\mathrm{DMPO}]_0}. \quad [16]$$

Consequently, the dependence of r^0/r on the initial concentration of p-cresol is expected to be linear, as will be confirmed below by the evaluation of the experimental results.

Equation [15] represents the formal first-order kinetic reaction with respect to the DMPO concentration in the photocatalytic system TiO_2–DMPO–p-cresol (15). Its solution for DMPO–OH$^\cdot$ formation, after a Taylor expansion of the exponential function and considering only the two first members of the expansion, can be written in the following form:

$$[\mathrm{DMPO{-}OH}^\cdot] = [\mathrm{DMPO}]_0\frac{K_{\mathrm{exp}}K_{\mathrm{DMPO}}}{1 + K_{\mathrm{DMPO}}[\mathrm{DMPO}]_0 + K_{\mathrm{CR}}[\mathrm{CR}]_0}t. \quad [17]$$

The relative intensity of the EPR signal of DMPO–OH$^\cdot$, $I_{\mathrm{EPR}}^{\mathrm{rel}}$, is proportional to DMPO–OH$^\cdot$ concentration:

$$I_{\mathrm{EPR}}^{\mathrm{rel}} = k_{\mathrm{EPR}}[\mathrm{DMPO{-}OH}^\cdot]. \quad [18]$$

Taking Eq. [18] into account, Eq. [17] can be reformulated as

$$I_{\mathrm{EPR}}^{\mathrm{rel}} = k_{\mathrm{EPR}}[\mathrm{DMPO}]_0\frac{k_{\mathrm{exp}}K_{\mathrm{DMPO}}}{1 + K_{\mathrm{DMPO}}[\mathrm{DMPO}]_0 + K_{\mathrm{CR}}[\mathrm{CR}]_0}t. \quad [19]$$

Thus, at a defined time t, a linear dependence of the reciprocal values of the relative intensity of the EPR signal, $I_{\mathrm{EPR}}^{\mathrm{rel}}$, on the various initial concentration of p-cresol, $[\mathrm{CR}]_0$, is expected if the Langmuir–Hinshelwood kinetic model is valid. This was experimentally verified, as shown below.

RESULTS AND DISCUSSION

In the first type of experiment (interrupted irradiation) on the photocatalytic system TiO_2–water–DMPO–p-cresol–oxygen, the EPR spectra of DMPO–OH$^\cdot$ were measured in the same sample after gradually increased irradiation time t_{ir}, as shown in Fig. 1. Then similar experiments taking samples with various initial p-cresol concentrations were carried out and the relative intensities of the EPR signal with increasing irradiation time were evaluated. Figure 2 illustrates three sets of such experiments at various initial p-cresol concentrations.

In the second type of experiment (continuous irradiation), the samples, again with various initial concentrations of p-cresol in TiO_2 suspensions containing DMPO, were continuously irradiated. Simultaneously, the change in EPR signal intensity of DMPO–OH$^\cdot$ was recorded with increasing irradiation time. Figure 3 represents four such selected sets of experiments at various initial p-cresol concentrations.

Figures 1–3 show that after quickly reaching the maximum value, $I_{\mathrm{EPR}}^{\mathrm{rel(max)}}$, of DMPO–OH$^\cdot$ formation, its concentration decreased with increasing irradiation time much faster than in the non-irradiated suspensions. The EPR signal decrease shown in Fig. 3 was fitted by the Marquardt minimization procedure of the least-squares method to the exponential function, the formal first-order rate constant was evaluated, and the half-life was calculated. The half-life of the DMPO–OH$^\cdot$ generated in the aqueous titanium dioxide suspension measured after irradiation-stop in our experiments was 14 min. Similar values were found in the literature (34). The mean half-life of

TABLE 1

Linear Dependence of the Reciprocal Values of the Relative Intensity of the EPR Signal on the Initial p-cresol Concentration after Various Irradiation Times t_{ir}[a]

Irradiation time (s)	Slope ($dm^3\ mol^{-1}$)	Intercept	Correlation coefficient
1	10.0 ± 1.2	0.009 ± 0.003	0.973
2	9.1 ± 0.5	0.008 ± 0.003	0.981
5	7.5 ± 0.3	0.001 ± 0.0005	0.986
8	6.3 ± 0.2	0.003 ± 0.0008	0.996
10	6.5 ± 0.2	0.001 ± 0.0005	0.994
15	6.9 ± 0.2	0.001 ± 0.0004	0.996
30	6.4 ± 0.2	0.002 ± 0.0008	0.995

[a] Taken from Fig. 2.

DMPO–OH· in the non-stop-irradiated photocatalytic systems is only 1 min.

The Langmuir–Hinshelwood kinetic model for the DMPO–OH· formation in the irradiated photocatalytic systems was considered here. In order to minimize the influence of DMPO–OH· decomposition and the changes in the oxygen concentration during irradiation, the experimental data were evaluated for the initial stage of reaction as follows:

(i) In systems with interrupted irradiation (Figs. 1 and 2), the dependences of the reciprocal values of the relative intensity of the EPR signal on the initial *p*-cresol concentration according to Eq. [19] were calculated for irradiation times shorter than 1 min.

(ii) The rate of the DMPO–OH· formation in the photocatalytic systems with continuous irradiation (Fig. 3) was evaluated as the initial rate (initial slope, r_{in}) (33) of the kinetic curve by means of the least-squares method.

Interrupted Irradiation

The values of the relative EPR intensities of DMPO–OH· at the applied irradiation times, t_{ir}, for the various initial *p*-cresol concentrations investigated were taken from the measured EPR spectra. Their reciprocal values $(I^{rel}_{EPR})^{-1}$ showed a linear dependence on the initial cresol concentration. The slope and the intercept of every line were determined by the least-squares method. Parameters of these evaluations at various irradiation times are summarized in Table 1. The mean values of their slopes and intercepts are 7.5 ± 1.4 dm^3 mol^{-1} and 0.003 ± 0.0012, respectively. The large differences in the values of the slopes and intercepts at the short irradaition periods (1 and 2 s) are attributed to the experimental errors in an exact determination of the relatively small line heights as well as to short irradiation times.

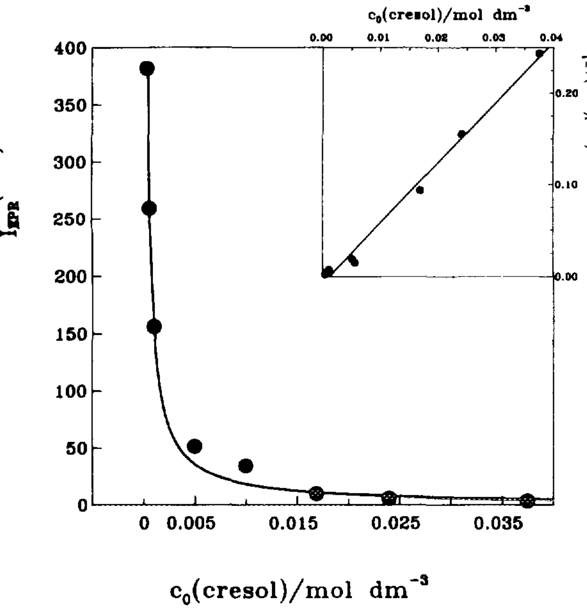


FIG. 4. Dependence of the maximum relative intensity of the EPR signal on the initial concentration of *p*-cresol in the photocatalytic systems using interrupted irradiation. Inset: Langmuir–Hinshelwood analysis of the same results (slope = 6.4 ± 0.2 dm^3 mol^{-1}, correl. coef. = 0.996).

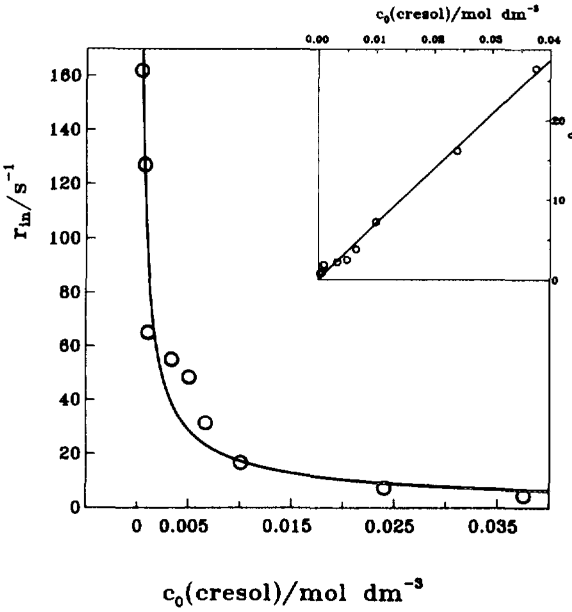


FIG. 5. Dependence of the initial rate of DMPO–OH· formation on the initial *p*-cresol concentration in continuously irradiated suspensions. Inset: Langmuir–Hinshelwood analysis of the same results (slope = 710 ± 20 dm^3 mol^{-1}, correl. coef. = 0.996).

The maximum relative intensities, $I^{rel(max)}_{EPR}$, of DMPO–OH· were read from experimental data and their

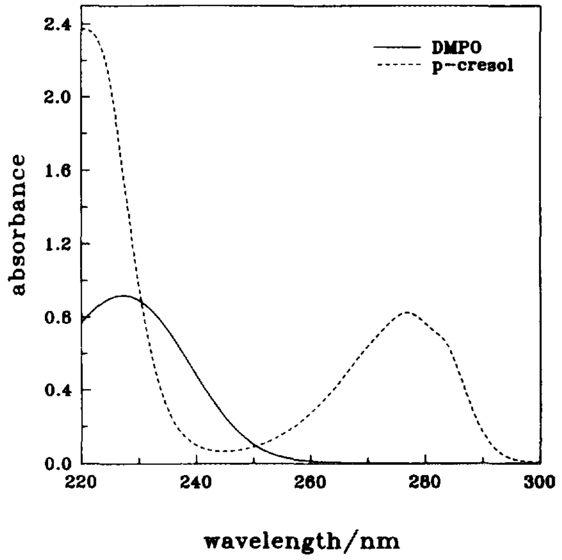


FIG. 6. UV spectra of *p*-cresol ([CR] = 1.0 mmol dm^{-3}, cell length 0.5 cm) and DMPO ([DMPO] = 1.0 mmol dm^{-3}, cell length 0.1 cm) in water.

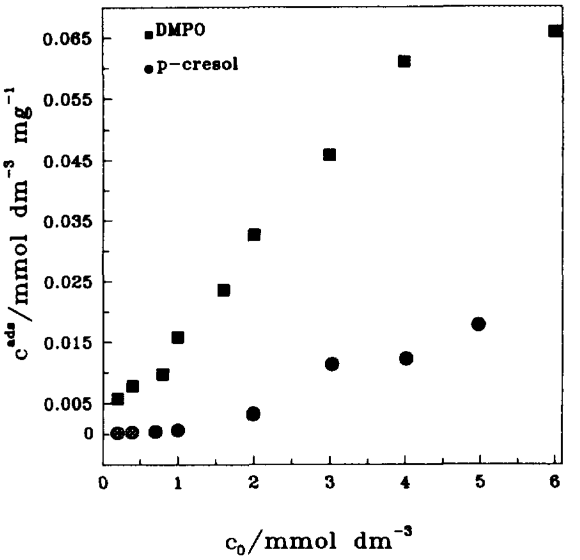


FIG. 7. Adsorption isotherms of p-cresol and DMPO on titanium dioxide ($[TiO_2]$ = 1 g dm^{-3}, temperature 295 K).

dependence on initial cresol concentration is shown in Fig. 4. A linear dependence was found representing the reciprocal values $(I_{EPR}^{rel(max)})^{-1}$ on the initial cresol concentration (inset, Fig. 4). The slope of 6.4 ± 0.2 dm^3 mol^{-1} and the intercept of 0.001 ± 0.0008 are close to those found above for various irradiation times. Therefore, it can be assumed that the evaluation of the maximum relative intensity is also sufficiently representative to characterize the photocatalytic system with the interrupted irradiation.

Continuous Irradiation

The dependence of the initial rates of DMPO–OH$^{\cdot}$ formation evaluated from experiments on the initial p-cresol concentration (according to Eq. [15]) is presented in Fig. 5. By acquisition of the evaluated initial rate ratios (r_{in}^0/r_{in}) on the initial p-cresol concentration, again a linear dependence was found with a slope of 710 ± 20 dm^3 mol^{-1} (inset, Fig. 5).

The similarity between the curves in Figs. 4 and 5 is striking. In both types of experiments, i.e., with interrupted and continuous irradiation, similar dependence of DMPO–OH$^{\cdot}$ formation on the initial p-cresol concentration is observed. In particular, the linear dependences of the DMPO–OH$^{\cdot}$ formation on the initial p-cresol concentration strongly support the assumed Langmuir–Hinshelwood kinetic model in the photocatalytic system investigated. The presence of the organic substrate (p-cresol) acts here as an inhibitor in the process of DMPO–OH$^{\cdot}$ formation (35).

Adsorption of p-cresol and DMPO on TiO_2

In order to confirm by the Langmuir–Hinshelwood model that competitive adsorption occurs between DMPO and p-cresol on one type of active TiO_2 surface site, adsorption measurements of both substrates in TiO_2 aqueous suspensions were carried out by UV spectroscopy. The UV spectra of DMPO and p-cresol in aqueous solutions are shown in Fig. 6. The absorbance at 227 nm was followed to determine the adsorption isotherm of DMPO and at 277 nm to obtain the adsorption isotherm of p-cresol, as well as to study the competitive adsorption between the two substrates. To obtain more reliable results, the spectra of each sample were accumulated (nine scans) and the concentration of the adsorbed p-cresol or DMPO per mg TiO_2, c^{ads}, was evaluated from the averaged spectrum using calibration curves. The dependence of c^{ads} on the initial substrate concentration c_0 is shown in Fig. 7.

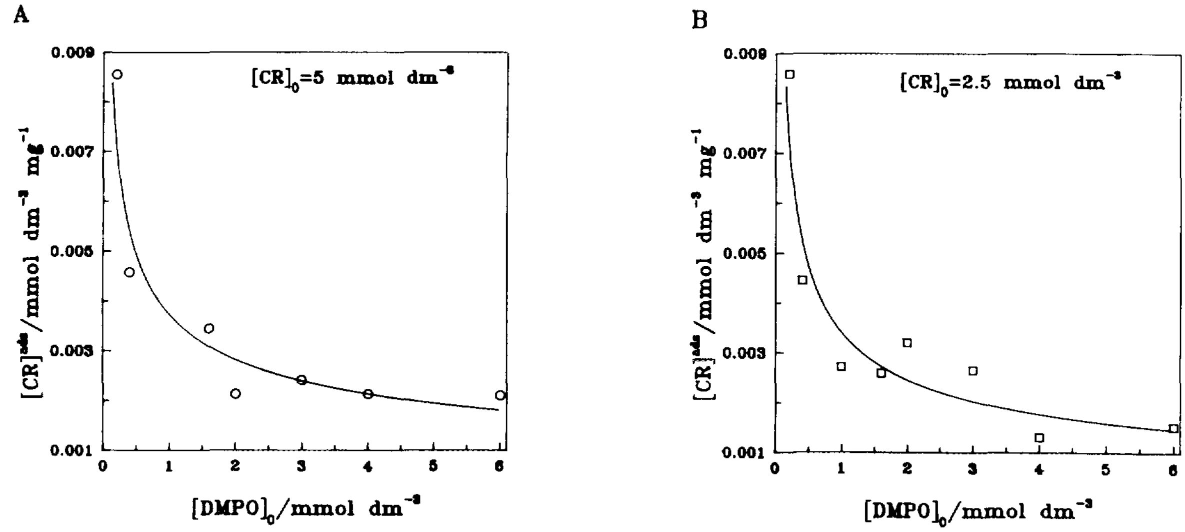


FIG. 8. Dependence of the adsorbed p-cresol concentration $[CR]^{ads}$ on the various initial DMPO concentrations $[DMPO]_0$ in the aqueous TiO_2 suspensions. (A): $[CR]_0$ = 5 mmol dm^{-3}; (B): $[CR]_0$ = 2.5 mmol dm^{-3}.

The adsorbed DMPO concentration on TiO_2 is significantly higher (about three times) than that of *p*-cresol.

Competitive adsorption was investigated in the systems with two relatively high concentrations of *p*-cresol ($[CR]_0 = 5$ m*M* and $[CR]_0 = 2.5$ m*M*). To samples of TiO_2 suspensions containing a constant *p*-cresol concentration, various amounts of DMPO were added. The samples were equilibrated for 6 h. Then TiO_2 was removed and the *p*-cresol concentration in the resulting solution was determined at 277 nm and thereby also the adsorbed amount of *p*-cresol on TiO_2. The results of such experiments are summarized in Figs. 8a and 8b. From this, it is evident that with increasing DMPO concentration, the concentration of *p*-cresol adsorbed on TiO_2 decreased. This confirms the competitive adsorption of both species on TiO_2.

CONCLUSIONS

The DMPO spin trap technique is shown to be a useful tool in kinetic studies of the photocatalytic system TiO_2–water–*p*-cresol–oxygen. The formation of hydroxyl radicals in the experimental conditions described was confirmed only in the presence of TiO_2. The reciprocal concentration values of DMPO–$OH^\cdot$ showed a linear dependence upon the initial *p*-cresol concentration, and the data obtained clearly fit the Langmuir–Hinshelwood kinetic model. The extent of adsorption of DMPO and of *p*-cresol was separately determined on TiO_2 in the concentration range 0–5 m*M* of substrates. The molar amount of DMPO adsorbed was about three times higher than that of *p*-cresol. At constant *p*-cresol concentrations (2.5 and 5 m*M*) and at variable DMPO concentration (10^{-4}–10^{-3} m*M*), competitive adsorption between the two species was found. This suggests that both types of species competitively adsorb onto the same sites of TiO_2. The adsorption of the organic substrate and consequently its heterogeneous photocatalytic degradation via hydroxyl radicals inhibit the DMPO–$OH^\cdot$ formation in the TiO_2 aqueous suspensions.

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