KINETICS OF DYE-SENSITIZED PHOTO-DEGRADATION OF AQUEOUS PHENOL

KEN-ICHI OKAMOTO, FUMIAKI HONDO,
AKIRA ITAYA AND SHIGEKAZU KUSABAYASHI

Department of Chemical Engineering, Yamaguchi University, Ube 755

The dye-sensitized photodegradation of aqueous phenol using rose bengal was carried out batch-wise in the chemical region by using an annular bubble-column photoreactor, to evaluate the use of sunlight in wastewater treatment. Effects of both the partial pressure of oxygen and the initial concentration of phenol, $[A]_0$, on the initial reaction rate were analyzed according to the reaction scheme including the quenching reaction of triplet dye $^3D^*$ with phenol, in order to determine the kinetic parameters. The reaction rate constant of phenol with singlet oxygen increased with increasing pH and was $2.66 \times 10^3 \text{ dm}^3/\text{mol} \cdot \text{s}$ at pH 10.3. The reaction quantum yield at pH 10.3 was limited to a maximum of 0.29 at $[A]_0 = 3 \times 10^{-3} \text{ mol/dm}^3$ for O_2 -bubbling and 0.13 at $[A]_0 = 1.4 \times 10^{-3} \text{ mol/dm}^3$ for air-bubbling by the quenching reaction of $^3D^*$ with phenol, of which the rate constant was $4.0 \times 10^3 \text{ dm}^3/\text{mol} \cdot \text{s}$. *p*-Benzoquinone, the primary main product, underwent further degradation with both alkaline and ground-state oxygen to yield final products such as carboxylic acids. The reaction curves were simulated closely up to high conversions by taking account of the quenching effect of both phenol and the quinone-type intermediate products on $^3D^*$.

Introduction

The dye-sensitized photooxidation of organic compounds has been the subject of much interest⁽¹⁴⁾, mainly because it may yield convenient ways of synthesizing fine chemicals. Most investigations, however, have dealt with either product distribution or apparent initial reaction rate without considering the oxygen interface mass transfer. Under some experimental conditions, the apparent reaction rate might be affected by the oxygen mass transfer, as pointed out by Brkic *et al.*^(2,3).

Recently, dye-sensitized photooxidation has become more important in view of the use of sunlight in wastewater treatment^(1,7,22,24). Many organic compounds resistant to biodegradation, such as phenols and lignins, can be oxidized in the presence of a photosensitizing dye, visible light and oxygen.

Phenol is a refractory and common compound in industrial wastes, and there is interest in developing a new type of chemical treatment method of phenol. In the present work, the dye-sensitized photodegradation of phenol in aqueous dilute solution was investigated in detail over a wide range of variables by use of an annular bubble-column photochemical reactor. The reaction was simulated up to high conversions by taking account of the quenching effect of both phenol and its intermediate products on the triplet sensitizer.

1. Experimental

The annular bubble-column photochemical reactor used is shown in Fig. 1. A tungsten-filament halogen lamp (Ushio Elec. Co., J220V 1000W) positioned at the axis of the column was usually operated at 110V. Two photocells (Hamamatsu Television Co., S641B) were positioned at the outer wall in order to monitor the light intensity emitted from the lamp during this study.

Rose bengal was used as a sensitizing dye, because of both its high stability and the high generation efficiency of singlet oxygen⁽¹⁴⁾. All reagents used were those of the highest grade available commercially,

Fig. 1 Annular bubble-column photochemical reactor

Received November 24, 1981. Correspondence concerning this article should be addressed to K. Okamoto. S. Kusabayashi is at Dept. of Appl. Chem., Osaka Univ., Suita 565. F. Hondo is with Sanyo Chemical Industries, Ltd., Kyoto 605.

which were purified by ordinary methods if necessary.

The reaction was carried out batchwise as follows. The reactor, into which gas was fed, was charged with 0.3 dm³ of aqueous solution containing both phenol and rose bengal. After the solution was brought to a desired temperature, the reaction was started by switching on the lamp. The reaction solution was kept at constant temperature by controlling temperatures of water jacket, feed gas, and a filter solution consisting of 1.17 mol/dm³ cupric chloride and 0.01 mol/dm³ potassium dichromate. During the reaction, pH of the solution was monitored with a pH meter and kept at the initially-set value by adding a 0.2N NaOH solution dropwise. At intervals, 2-ml samples were withdrawn and analyzed for concentration of phenol and its degradation products by use of a high-performance liquid chromatograph (Hitachi, 635-A) with a column packed with ODS gel. An aqueous solution containing 50% methanol and 1% acetic acid was used as an eluting solvent for analysis of phenol. An aqueous solution of 0.2% acetic acid was used for analysis of the products. The products were identified on the basis of both retention time and the intensity ratio of the signals at two different wavelengths of each authentic sample.

The experimental conditions used are listed in Table 1.

2. Results and Discussion

2.1 Volumetric rate of light absorption

The point light intensity within the reactor charged with 0.3 dm³ of water was measured by a photocell. Being constant within $\pm 5\%$ in the axial direction, the light intensity followed the radial light model⁽⁴⁾ in the radial direction.

The spectral distribution F_λ of the lamp working at voltage E was measured by using an optical system composed of the lamp, a convex lens, a monochrometer and a photocell. This optical system was previously corrected spectrally by operating the lamp at the regular voltage*. A typical example of F_λ is shown in Fig. 2, where it is given as the ratio of the light intensity at λ nm to that at 700 nm. Then, by neglecting the effects of reflection and refraction, the light intensity $I_{w,\lambda}$ at the inner wall of the reactor without filter solution can be written as $I_{w,\lambda} = I_{w,700} F_\lambda$.

In the case of no concentration distribution, the mean volumetric rate of light absorption, $\bar{I}_a$, is given by Eq. (1) according to the radial light model.

$$\bar{I}_a = \left(\frac{2 \times 10^3 I_{w,700} r_1}{r_2^2 - r_1^2} \right) \int_{\lambda} T_\lambda F_\lambda [1 - \exp \{-\mu_\lambda(r_2 - r_1)\}] d\lambda \quad (1)$$

* The color temperature of the lamp working at the regular voltage (220 V) is 3050 K.

Table 1 Experimental conditions

Initial concentration of phenol, $[A]_0$	$(0.05-5) \times 10^{-3}$ mol/dm ³
Concentration of dye, $[D]$	$(0.6-1.8) \times 10^{-5}$ mol/dm ³
Reaction volume	0.3 dm ³
Reaction time	6-120 min
pH	6.5-10.7
Temperature	5-40°C
Working voltage of lamp, E	80-130 V
Superficial gas velocity, u_g	0.34-0.8 cm/s
Partial pressure of oxygen, P_{O_2}	0.08-1 atm
Speed of stirring paddle	0-120 rpm

Fig. 2 F_λ , T_λ , and $\epsilon_{\lambda,D}$

where r_1 and r_2 are the inner and outer radii of the reactor, respectively, T_λ is transmittance of the filter solution shown in Fig. 2, and μ_λ is the attenuation coefficient of the reaction solution.

To determine $I_{w,700}$, the Reinecke salt actinometer reaction⁽²⁶⁾ was carried out in the same reactor. The volume of 0.3 dm³ of $(0.6-2) \times 10^{-2}$ mol/dm³ solution of Reinecke salt was irradiated for 10 min with bubbling nitrogen ($u_g = 0.39-0.65$ cm/s). The volumetric rate of the actinometer reaction, Ω_R , was determined for each concentration of the solution at $E = 110V$; for example, $(2.16 \pm 0.08) \times 10^{-6}$ mol/dm³·s for 2×10^{-2} mol/dm³. Ω_R is expressed by Eq. (2).

$$\Omega_R = \left(\frac{2 \times 10^3 I_{w,700} r_1}{r_2^2 - r_1^2} \right) \int_{\lambda} \phi_{R,\lambda} T_\lambda F_\lambda \times [1 - \exp \{-\mu_{R,\lambda}(r_2 - r_1)\}] d\lambda \quad (2)$$

where $\phi_{R,\lambda}$ is quantum yield of the reaction. The integral term of Eq. (2) can be calculated by using both the data of $\phi_{R,\lambda}$ and molar extinction coefficient $\epsilon_{R,\lambda}$ ⁽²⁶⁾ and those of T_λ shown in Fig. 2. Thus, $I_{w,700}$ was determined to be $(6.56 \pm 0.23) \times 10^{-9}$ ein/cm²·nm·s for $E = 110V$, irrespective of both u_g and concentration of the solution.

Now, the mean volumetric rate of light absorption of rose bengal, $\bar{I}_{a,D}$, in the sensitized reaction system can be calculated by Eq. (1), and is shown in Fig. 4.

2.2 Initial rate of sensitized photodegradation

It was first confirmed that phenol was effectively

Fig. 3 Effect of u_g on both $\Omega_{A,0}$ and $k_L a$

Fig. 4 Effect of $[D]$ on $\Omega_{A,0}$, $I_{a,D}$ and $\phi_{r,A}$

Fig. 5 Effect of E on both $I_{a,D}$ and $\phi_{r,A}$

degraded only in the presence of rose bengal, dissolved oxygen, and visible light. Rose bengal bleached at a slow rate of about 6×10^{-8} mol/dm³·hr during the reaction. However, this is neglected in this paper.

The initial reaction rate $\Omega_{A,0}$ was determined from a curve of phenol concentration $[A]$ vs. reaction time t for the early stage of the reaction, in order to eliminate any complexed effect of the products.

Figure 3 shows the effect of superficial gas velocity u_g on $\Omega_{A,0}$. Above 0.35 cm/s, $\Omega_{A,0}$ did not depend on either u_g or the speed of a stirring paddle from 0 to 120 rpm. The volumetric coefficient for liquid-phase mass transfer, $k_L a$, was measured by the absorption of CO₂ into Na₂CO₃-NaHCO₃ solution²³, and converted into that for the O₂-water system under the assumption of $k_L a \propto (D_L \varepsilon_g^2 / d_p)^{1/2}$, where D_L is molecular diffusivity in liquid, ε_g gas hold-up and d_p volume surface mean diameter of bubbles. The result is shown in Fig. 3. The ratio of bulk concentration of oxygen to interface concentration, $[^3\text{O}_2]_i / [^3\text{O}_2]_b$, was evaluated from the $k_L a$ data to be 0.98 and 0.93 at $u_g = 0.44$ cm/s for P_{O_2} of 1 atm and 0.1 atm, respectively. It was thus demonstrated that oxygen mass transfer did not affect $\Omega_{A,0}$ at u_g more than 0.44 cm/s under the present experimental conditions. The results to be mentioned below were obtained for u_g values greater than 0.44 cm/s without the stirring paddle.

The effect of $\bar{I}_{a,D}$ on $\Omega_{A,0}$ was examined by changing either E or the dye concentration $[D]$. As is shown in Figs. 4 and 5, the reaction yield $\phi_{r,A}$ ($= \Omega_{A,0} / \bar{I}_{a,D}$) was constant, being independent of both $[D]$ and E . The results reported below were obtained for $[D] = 9.3 \times 10^{-6}$ mol/dm³ and $E = 110$ V.

The effects of initial phenol concentration $[A]_0$ and partial pressure of oxygen P_{O_2} on $\Omega_{A,0}$ are shown in Figs. 6 and 7, respectively.

For dye-sensitized photooxidation, the following reaction scheme has been generally accepted^{14,25}.

where B is the primary product, ϕ_T is the generation quantum yield of the triplet dye ${}^3D^*$, and k_0 , k_t , k_r , and k_d are the rate constants of each elementary reaction. Under the steady-state approximation of the intermediate species, the reaction rate Ω_A is expressed by Eq. (3).

$$\begin{aligned} \Omega_A &= -d[A]/dt = k_L a ([^3\text{O}_2]_i - [^3\text{O}_2]) \\ &= \left(\frac{\phi_T \bar{I}_{a,D} k_t [^3\text{O}_2]}{k_0 + k_t [^3\text{O}_2]} \right) \left(\frac{[A]}{\beta + [A]} \right) \end{aligned} \quad (3)$$

where β is the reactivity ratio ($= k_d / k_r$).

The values of ϕ_T , k_t , and k_0 for rose bengal in aqueous solution are reasonably assumed to be nearly equal to those in methanol solution (0.77 , 1.2×10^9 dm³/mol·s, and 6.5×10^3 s⁻¹, respectively)⁹. It is

(1)–(4): Calculated from Eq. (4);
(5): Calculated from Eq. (3)

Fig. 6 Relation between $\Omega_{A,0}$ and $[A]_0$

estimated from Eq. (3) using these values that $\Omega_{A,0}$ should not depend on $[^3\text{O}_2]$ at values higher than 10^{-4} mol/dm³. This is quite in contrast to the result shown in Fig. 7. The following additional reaction should, therefore, be considered in the case of phenol.

where $k_{q,A}$ is the rate constant. This is a kind of quenching reaction of $^3D^*$ with phenol, because of the very fast direct back-reaction between the product radicals¹⁰⁾. Now, Eq. (3) is modified to Eq. (4).

$$\Omega_A = \left(\frac{\phi_T \bar{I}_{a,D} k_t [^3\text{O}_2]}{k_0 + k_t [^3\text{O}_2] + k_{q,A} [A]} \right) \left(\frac{[A]}{\beta + [A]} \right) \quad (4)$$

Equation (4) is rearranged to Eq. (5).

$$\frac{1}{\Omega_A} = \left\{ \frac{\beta + [A]}{\phi_T \bar{I}_{a,D} k_t [A]} \right\} \left\{ k_t + \frac{k_0 + k_{q,A} [A]}{[^3\text{O}_2]} \right\} \quad (5)$$

The plots of $1/\Omega_{A,0}$ vs. $[^3\text{O}_2]^{-1}$ at $[A]_0 = 1 \times 10^{-3}$ mol/dm³ gave a straight line, as shown in Fig. 7. The $k_{q,A}$ was determined to be 4.0×10^8 dm³/mol·s according to Eq. (5), using for k_0 and k_t 6.5×10^3 s⁻¹ and 1.2×10^9 dm³/mol·s, respectively⁹⁾.

Equation (4) is also rearranged to Eq. (6).

$$\frac{k_t [^3\text{O}_2]}{(k_0 + k_t [^3\text{O}_2] + k_{q,A} [A]) \Omega_A} = \frac{1 + \beta/[A]}{\phi_T \bar{I}_{a,D}} \quad (6)$$

The plots of $k_t [^3\text{O}_2]/(k_0 + k_t [^3\text{O}_2] + k_{q,A} [A]) \Omega_{A,0}$ vs. $[A]_0^{-1}$ at $[^3\text{O}_2] = 1.224 \times 10^{-3}$ mol/dm³ gave a straight line for each pH, as shown by a typical example in Fig. 8. The ϕ_T and β were determined according to Eq. (6). The k_r was determined from the β value using k_d in water, 5×10^{-5} s⁻¹^{18,27)}. It is noted that the calculated value (7.5×10^{-5} dm³ s/ein) of $(\beta + [A]_0)/(\phi_T \bar{I}_{a,D} [A]_0)$ for pH 10.3 and $[A]_0 = 1 \times 10^{-3}$ mol/dm³ is

Fig. 7 Relation between $\Omega_{A,0}$ and P_{O_2} , and plots of $\Omega_{A,0}^{-1}$ vs. $[^3\text{O}_2]^{-1}$ according to Eq. (5)

Fig. 8 Plots of $k_t [^3\text{O}_2]/(k_0 + k_t [^3\text{O}_2] + k_{q,A} [A]) \Omega_{A,0}$ vs. $[A]_0^{-1}$ according to Eq. (6)

Table 2 Kinetic parameters determined or cited in the present paper

$k_0 = 6.5 \times 10^3$ s ⁻¹ , ref. 9)
$k_t = 1.2 \times 10^9$ dm ³ /mol·s, ref. 9)
$\phi_T = 0.83$
$k_d = 5.0 \times 10^5$ s ⁻¹ , refs. 18) and 27)
$\beta = 1.88 \times 10^{-8}$, 8.15×10^{-3} , and 2.56×10^{-2} mol/dm ³ for pH 10.3, 9, and 8, respectively
$k_r = 2.66 \times 10^3$, 6.13×10^7 , and 1.95×10^7 dm ³ /mol·s for pH 10.3, 9, and 8, respectively
$k_{q,A} = 4.0 \times 10^8$ dm ³ /mol·s
$k_{q,Q} = 3.5 \times 10^9$ dm ³ /mol·s
$\Delta E_a = 17$ kJ/mol
Maximum value of $\phi_{r,A} = 0.29$ and 0.13 for $P_{O_2} = 1$ and 0.21 atm, respectively

consistent with the value observed as the intercept of the straight line shown in Fig. 7.

The kinetic parameters thus determined are listed in Table 2. Using them, the curves of $\Omega_{A,0}$ vs. $[A]_0$ for each pH were calculated from Eq. (4) and are shown in Fig. 6. The calculated curves (1)–(4) agree well with the experimental data. It is noted that $\Omega_{A,0}$ decreases with an increase of $[A]_0$ after reaching

(a) —○—: phenol, —●—: BQ, ---△---: HQ, ---▲---: HBQ, —□—: DHBQ, ---■---: MA

(b) —○—: acid, amount of which was determined from NaOH added to keep pH of solution constant; —●—: carbonyl group, amount of which was determined from consumed amount of 1,2-di-nitrophenylhydrazine; ---△---: unknown product X; ---▲---: unknown product having retention time of 4.4 min.

Fig. 9 Variation of concentration of products with reaction time at pH 10.3

a maximum rate. At pH 10.3, the maximum value of $\phi_{r,A}$ is 0.29 at $[A]_0 = 3 \times 10^{-3}$ mol/dm³ for O₂-bubbling and 0.13 at $[A]_0 = 1.4 \times 10^{-3}$ mol/dm³ for air bubbling. The hypothetical curve of $\Omega_{A,0}$ vs. $[A]_0$ for the case of no quenching of ³D* with phenol was also calculated from Eq. (3) and is shown by the dotted line (5) in Fig. 6. Comparison between curves (1)–(4) and (5) shows clearly how much the quenching effect of phenol reduces the reaction rate.

The reactivity of phenol with ¹O₂ was found to increase with increasing pH. The β was correlated to pH by Eq. (7).

$$\beta = 2.4 \times 10^2 \exp(-1.14 [\text{pH}]) \quad (7)$$

The β value for pH 7 is evaluated to be 0.06 mol/dm³, which gives the k_r value of 8×10^6 dm³/mol·s. This k_r value is larger than those observed for 2,6-di-*tert*-butylphenol²⁵⁾ and α -naphthol¹⁹⁾ in methanol solution (1.0×10^6 and 7.8×10^5 dm³/mol·s, respectively). The k_r value (2.7×10^8 dm³/mol·s) of phenol for pH 10.3 is comparable to those of N₃¹²⁾ and 9,10-anthracene-propionic acid¹⁶⁾ (2.8×10^8 and 8.2×10^7 dm³/mol·s, respectively), which are typical quenchers of ¹O₂ in aqueous solution. Thus, phenol at pH 10.3 or phenolate ion was found to be very reactive with ¹O₂.

The temperature dependence of $\Omega_{A,0}$ was examined in the range of 5 to 40°C at pH 9 and $[A]_0 = 5 \times 10^{-4}$ mol/dm³. The $\Omega_{A,0}$ had a small activation energy ΔE_a of 17 kJ/mol.

2.3 Products and reaction pathway

The reaction products identified from liquid chromatograms were *p*-benzoquinone (abbreviated as BQ), hydroquinone (HQ), catechol (CC), 2-hydroxyhydroquinone (HHQ), 2-hydroxy-1,4-benzoquinone (HBQ), 2,5-dihydroxy-1,4-benzoquinone (DHBQ), and maleic acid (MA). A relatively large peak was observed at a retention time of 20 min and was attributed to an unknown product X. Many peaks were also observed in the range of retention time less than 7 min. These peaks were enhanced with increasing reaction time and were attributed to final products being very polar like carboxylic acid.

Figures 9 (a) and (b) show the variation in concentration of the products with reaction time at pH 10.3. These figures show that the primary major product is BQ and the primary minor one HQ. Although a trace of CC was also formed as the primary product, the combined amount of BQ and HQ agreed closely with the amount of consumed phenol up to a conversion of 40% at pH 9 and of 25% at pH 10.3, respectively. For this initial period, the concentration ratio of HQ to BQ remained constant at 0.09 for pH 9 and 0.04 for pH 10.3, respectively. A trace of HHQ less than 2×10^{-6} mol/dm³ was observed until BQ disappeared completely. HHQ, HBQ, DHBQ, and the unknown product X are the intermediate products, which change to the final products by further oxidation. It is noted that no coupling products such as 4,4'-dihydroxybiphenyl or 4,4'-diphenylquinone of phenoxy radicals were formed in the present case, in contrast to the case of alkyl-substituted phenols^{17,21,25)}.

Judging from the case of 2,5-di-*tert*-butylhydroquinone²⁰⁾, HQ seems to produce BQ by further oxidation.

tion with $^1\text{O}_2$. It has been reported that BQ quenches the triplet dyes but does not react with $^1\text{O}_2$ ⁸⁾. It is well known that BQ undergoes a complicated degradation reaction in aqueous alkaline solution¹³⁾. Photolysis of aqueous BQ solution has been reported to produce HHQ as the primary product independent of pH^{11,15)}. HHQ is unstable in alkaline solution, and is oxidized to HBQ and further to DHBQ^{11,15)}. HBQ polymerizes at high concentrations to humic acid and DHBQ gives pyruvic acid in alkaline solution^{5,6)}.

To make clearer the reaction pathway, BQ, the primary main product, was subjected to rose-bengal-sensitized photodegradation. By bubbling O_2 gas at pH 10.3, a dilute BQ solution gave no precipitate and remained clear, although the concentrated solution ($1 \times 10^{-2} \text{ mol/dm}^3$) gave a brown polymeric precipitate. The following results were obtained for a solution of $3 \times 10^{-4} \text{ mol/dm}^3$, the maximum concentration observed for the photodegradation of phenol shown in Fig. 9 (a). In the dark reaction, BQ disappeared at an initial rate of 2×10^{-8} and $2 \times 10^{-7} \text{ mol/dm}^3 \cdot \text{s}$ at pH 9 and 10.3, respectively. In the photoreaction ($\bar{I}_{a,D} = 4.6 \times 10^{-6} \text{ ein/dm}^2 \cdot \text{s}$), the initial rate increased by a factor of 2 at both pH 9 and pH 10.3. The products observed were the same as mentioned above for phenol except BQ and HQ. The variation of their concentration with reaction time in the photoreaction was also similar to that observed for phenol. Both acids and carbonyl group were formed at a much slower rate in the dark-reaction than in the photoreaction. When the illuminated solution was bubbled with N_2 gas instead of O_2 , BQ disappeared at the almost same rate, but both the disappearance of the intermediate products and the formation of acids and carbonyl group were much slowed.

From these results and the references mentioned above, the reaction pathway shown in Fig. 10 seems to be the most likely.

2.4 Variation of phenol concentration with reaction time

Variation of phenol concentration with reaction time (called reaction curve below) was measured up to high conversions. As shown in Fig. 11, phenol disappeared at a much lower rate than that predicted from Eq. (4), suggesting that the reaction was retarded by products such as BQ.

When a substrate Q quenches the triplet dye at a quenching constant $k_{q,Q}$, Eq. (4) must be modified to Eq. (8).

$$\Omega_A = \left(\frac{\phi_T \bar{I}_{a,D} k_t [^3\text{O}_2]}{k_0 + k_t [^3\text{O}_2] + k_{q,A} [A] + k_{q,Q} [Q]} \right) \left(\frac{[A]}{\beta + [A]} \right) \quad (8)$$

The quenching experiments showed that addition

Fig. 10 Reaction pathway of dye-sensitized photodegradation

Broken lines ((4) and (6)) were calculated from Eq. (4), other lines from Eq. (10). (1), (2), (3), and (7): $\alpha = 0.65$, (5): $\alpha = 0$, (8): $\alpha = 1$ and $k_{q,A} = 0$, (9): $\beta = 1.50 \times 10^{-3} \text{ mol/dm}^3$ and $\alpha = 0.85$

Fig. 11 Comparison between experimental and calculated reaction curves

of BQ ($5 \times 10^{-4} \text{ mol/dm}^3$) reduced $\Omega_{A,0}$ for pH 9 by a factor of 2. The $k_{q,Q}$ value of BQ was thus determined to be $3.5 \times 10^9 \text{ dm}^3/\text{mol} \cdot \text{s}$.

As DHBQ, the unknown product X and their further-oxidation products consume $^1\text{O}_2$ to produce the final products as shown in Fig. 10, the fraction, $[A]/(\beta + [A])$, by which $^1\text{O}_2$ formed reacts with phenol must be replaced by the following one: $[A]/(\beta + [A] + k_{r,Y}[Y]/k_{r,A})$, where $[Y]$ is the total concentration of the intermediate products reacting with $^1\text{O}_2$ and $k_{r,Y}$ their average rate constant. However, the correction term, $k_{r,Y}[Y]/k_{r,A}$, can be neglected in the first approximation, because it is safely assumed to be less than 10% of the first term β in the present experimental range. Then, Eq. (8) was used under the following three assumptions, in order to explain the experimental reaction curves. First, the effect due to

Solid lines were calculated from Eq. (12).

Fig. 12 Relation between K and $[A]_0$

formation of HQ and CC was neglected. Second, all the intermediate products which act as a quencher of the triplet dye were assumed to have the same quenching constant as observed for BQ. Thus, $[Q]$ stands for the total concentration of these intermediate products. Third, $[Q]$ was assumed to be expressed by Eq. (9) for simplification.

$$[Q] = (1 - \alpha)([A]_0 - [A]) \quad (9)$$

where α is an experimental constant. Then, Eq. (8) can be integrated to give Eq. (10).

$$\begin{aligned} t\phi_T \bar{I}_{a,D} k_t [^3O_2] = & \{k_0 + k_t [^3O_2] + k_{q,q}(1 - \alpha)[A]_0\} \\ & \times \{\beta \ln([A]_0/[A]) + \{k_0 + k_t [^3O_2] \\ & + k_{q,q}(1 - \alpha)([A]_0 - \beta) + \beta k_{q,A}\} \\ & \times ([A]_0 - [A]) + \{k_{q,A} - k_{q,q}(1 - \alpha)\} \\ & \times ([A]_0^2 - [A]^2)/2 \} \quad (10) \end{aligned}$$

All the kinetic parameters determined or cited in the present paper are listed in Table 2. For pH 9, the α value was taken as zero, because the quinone-type products detected amounted to more than 80% of consumed phenol during the reaction for 1 hr, and the reaction curve calculated from Eq. (10) agreed well with the experimental one, as shown in Fig. 11. For pH 10.3, the α value was taken as 0.65 to get the calculated reaction curves to fit the experimental ones. This α value is reasonable, judging from Figs. 9 (a) and (b). It is noted that Eq. (10) gave excellent agreement between calculated and experimental reaction curves by using the same α value regardless of $[A]_0$.

Sargent and Sanks have reported that the reaction curves for the methylene-blue-sensitized photodegradation of cresol follow Eq. (11) closely²²⁾, although the reaction is not simple first-order.

$$\log([A]_0/[A]) = K \cdot t \quad (11)$$

In the present case, the reaction curves also followed Eq. (11) fairly well, although the apparent rate constant K observed depended on $[A]_0$, as shown in Fig. 12. This is explained by the fact that the first term in Eq. (10) is more important than the other terms,

especially in the range of the low $[A]_0$. If the second and third terms in Eq. (10) are neglected, K will be given by Eq. (12).

$$\begin{aligned} K = & \phi_T \bar{I}_{a,D} k_t [^3O_2] / 2.303 \beta \{k_0 + k_t [^3O_2] \\ & + k_{q,q}(1 - \alpha)[A]_0\} \quad (12) \end{aligned}$$

Figure 12 shows that the dependency of K on $[A]_0$ follows Eq. (12) approximately.

2.5 A few problems related to practical application

Comparison between reaction curves (7) and (8) in Fig. 11 shows clearly that the quenching effect of phenol and the quinone-type intermediate products on $^3D^*$ reduces significantly the efficiency of photo-degradation of phenol in the case of air-bubbling. The rate of aerobic dark-degradation of the quinone-type intermediate products increases rapidly with increasing pH of the solution. Therefore, the efficiency of photo-degradation of phenol is much improved by raising pH of the solution a little more from 10.3, as shown by reaction curve (9) in Fig. 11.

A set of several different dyes having both high ϕ_T values and low $k_{q,A}$ values should be chosen in order to utilize the entire effective wavelength region of irradiated light. These dyes should be used in immobilized form for the following reasons. Heterogeneous sensitizers are expected to be stable toward bleaching. They can be easily removed from the solution and can be reused with little loss in efficiency. Kinetic studies of the photodegradation of phenol using heterogeneous sensitizers are in progress.

Conclusions

The dye-sensitized photodegradation of aqueous phenol was carried out in the chemical region, and both the kinetic parameters listed in Table 2 and the reaction pathway shown in Fig. 10 were elucidated. The $\phi_{r,A}$ at pH 10.3 was limited to a maximum of 0.29 for O_2 -bubbling and 0.13 for air-bubbling by the quenching effect of phenol on $^3D^*$. The reaction curves were simulated closely up to high conversions by Eq. (10), where the quenching effect of both phenol and the quinone-type intermediate products on $^3D^*$ was taken into account. From the viewpoint of application to wastewater treatment, it is important to carry out the reaction in the higher pH region by using a set of suitable sensitizing dyes in immobilized form.

Nomenclature

$[A]$	= concentration of phenol	[mol/dm ³]
$[D]$	= concentration of dye	[mol/dm ³]
E	= working voltage of lamp	[V]
F_λ	= ratio of light intensity at λ nm to that at 700 nm	[—]
I_a	= mean volumetric rate of light absorption	[ein/dm ³ ·s]

$I_{w,\lambda}$	= light intensity of λ nm at inner wall of reactor	[ein/cm ² ·s·nm]
K	= apparent first-order rate constant	[s ⁻¹]
k_d, k_0	= first-order rate constant	[s ⁻¹]
k_q, k_r, k_t	= second-order rate constant	[dm ³ /mol·s]
k_{La}	= volumetric coefficient for liquid-phase mass transfer	[s ⁻¹]
[³ O ₂]	= concentration of ground-state oxygen	[mol/dm ³]
P_{O_2}	= partial pressure of oxygen	[atm]
[Q]	= concentration of quencher	[mol/dm ³]
r	= radius	[cm]
T_λ	= transmittance of filter solution	[—]
t	= reaction time	[s] or [min]
u_g	= superficial gas velocity	[cm/s]
[Y]	= total concentration of intermediate products reacting with ¹ O ₂	[mol/dm ³]
α	= experimental constant	[—]
β	= reactivity ratio (= k_d/k_r)	[mol/dm ³]
ΔE_a	= activation energy of $\Omega_{A,0}$	[kJ/mol]
ϵ	= molar extinction coefficient	[dm ³ /mol·cm]
ϕ	= quantum yield	[—]
μ	= attenuation coefficient	[cm ⁻¹]
Ω	= volumetric reaction rate	[mol/dm ³ ·s]
<Subscripts>		
0	= initial value	
1	= inner wall	
2	= outer wall	
A	= phenol or substrate	
D	= dye	
i	= interface	
Q	= quencher	
R	= Reinecke salt actinometer	
r	= dye-sensitized reaction	
T	= triplet state	
λ	= wavelength	

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(Presented in part at the 14th Autumn Meeting of The Soc. of Chem. Engrs., Japan, at Yokohama, October 1980.)