Electron Spin Resonance Studies on the Mechanism of the Formation of *p*-Benzosemiquinone Anion over Manganese Dioxide

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The formation of *p*-benzosemiquinone anion radical in a hydroquinone aqueous solution over manganese dioxide has been studied by e.s.r. spectroscopy. The rate of the formation of the radical strictly obeyed equation (i)

$$d[SA]/dt = k(b[HQ]_0 - [SA])(c[MnO_2]_0 - [SA]) \qquad (i)$$

where k, b, and c are constants, $[MnO_2]_0$ is the MnO_2 weight : liquid volume ratio, and $[HQ]_0$ and [SA] are the initial concentrations of hydroquinone and semiquinone anion radical, respectively. The following reaction mechanism is proposed. The surface species MnO_2^* abstracts a hydrogen atom from hydroquinone to form a neutral semiquinone radical which desorbs into the liquid phase and is converted into semiquinone anion radical, while the surface species MnO_2^* is deactivated and reduced to $Mn(OH)_2^*$. The number of surface species, MnO_2^*, is determined as 7.7×10^{18} m^{-2}.

MANGANESE DIOXIDE is known as a mild, selective oxidant of many organic compounds.[1] Recently manganese dioxide has been also used as a heterogeneous catalyst in the liquid-phase autoxidation of hydrocarbons.[2-5] Various mechanisms on the oxidations by manganese dioxide were proposed from the beginning since Ball *et al.*[6] suggested that the oxidation of vitamin A with manganese dioxide occurred on the surface of the dioxide. Pratt *et al.*[7] suggested a reaction mechanism for the oxidation of diarylmethanes with manganese dioxide involving the elementary steps (1) and (2) on the dioxide surface.

$$Ar_2CH_2 + O{=}Mn{=}O \longrightarrow Ar_2CH\cdot + HO{-}Mn{=}O \qquad (1)$$

$$Ar_2CH_2 + HO{-}Mn{=}O \longrightarrow Ar_2CH\cdot + HO{-}Mn{-}OH \qquad (2)$$

Similar mechanisms involving free radical intermediates for the oxidation of hydrocarbons, amines, and alcohols by manganese dioxide have been proposed.[6-12] However, the presence of free radicals in the system has not

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been confirmed and the reaction mechanisms have not yet been fully elucidated.

We have found that *p*-benzosemiquinone anion radicals are observed in the liquid phase by e.s.r. or u.v. spectroscopy when an aqueous solution of hydroquinone is passed through a column of manganese dioxide, and have studied the kinetics of the formation of semiquinine anions using a flow technique.[13,14] A mechanism for this reaction has been proposed such that Mn^{IV} on the surface of manganese dioxide is reduced to Mn^{II} with hydroquinone from which semiquinone anion is formed *via* a neutral semiquinone radical.[14] However, the elementary steps on the solid surface have not been made clear.

In the present study, we have attempted to provide further insight into the mechanism by investigating in more detail the kinetics of the formation of semiquinone anion. A reaction mechanism has been proposed involving the elementary steps on the solid surface, analogous to that proposed by Pratt *et al.*,[7] which is consistent with the kinetic results. The number of active surface species for the formation of semiquinone anion will be determined.

EXPERIMENTAL

The oxidation of hydroquinone with manganese dioxide in aqueous solution was carried out in a 2 dm^3 reaction bottle immersed in a temperature-controlled bath. Nitrogen gas was bubbled through an aqueous solution of hydroquinone for 1 h before manganese dioxide powder was added to the solution and the oxidation was started under nitrogen. An e.s.r. sample cell placed in the e.s.r. cavity was connected to the reaction bottle. The dead volume between the outlet of the reaction bottle and the e.s.r. sample cell was 2—3 cm^3. During the reaction, the small part of the reactant solution (*ca.* 3 cm^3) was flowed through the e.s.r. sample cell and then the flow was stopped, when the e.s.r. measurements were carried out with a JEOL X-band spectrometer (JES-PE-1X) with 100 kHz magnetic field modulation. During the e.s.r. measurements, the decay of semiquinone anion in the liquid phase was negligible.[13,14] The radical concentration was determined by comparing the absorption area of the radical and that of 1,1-diphenyl-2-picrylhydrazyl in benzene. Most experiments were carried out at 298 K.

Manganese dioxide and hydroquinone were obtained from Wako Pure Chemicals. The BET surface area of manganese dioxide powder used was 14.3 m^2 g^{-1}. *X*-Ray powder diffraction photography revealed that the manganese dioxide used was the β-form. Preliminary experiments confirmed that the reactions are not diffusion controlled.

RESULTS

The e.s.r. spectrum, obtained from the oxidation of hydroquinone with manganese dioxide, consists of five lines with an intensity ratio of 1 : 4 : 6 : 4 : 1. The hyperfine coupling constant (0.238 mT) and the *g* value (2.0046) agree with those of *p*-benzosemiquinone anion radical in the literature.[14-17] When manganese dioxide is added to an aqueous solution of hydroquinone, semiquinone anion radical is observed and the radical concentration [SA] increases with time to reach a steady value $[SA]_\infty$. Typical examples of the kinetic results are shown in Figure 1. The decay of the radical in the liquid phase during the reaction is negligible.[13,14]

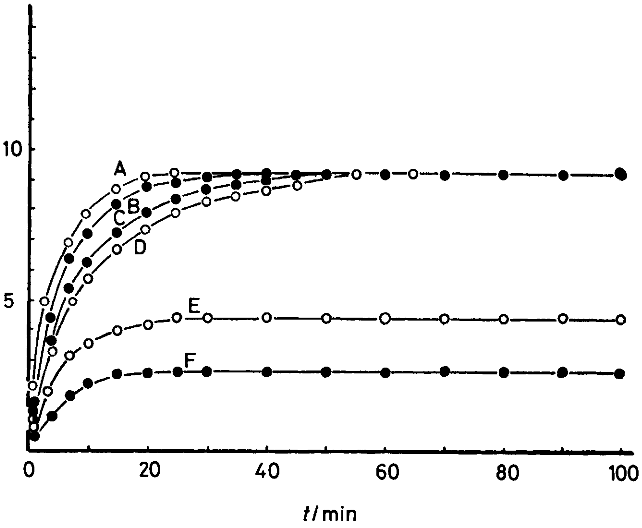

FIGURE 1 Concentration of semiquinone anion [SA] *versus* reaction time at 298 K. Initial concentration of hydroquinone: A 40; B 30; C 20; D 7.5; E 5; F 3mM; initial MnO_2 weight : liquid volume ratio 0.25 g l^{-1}

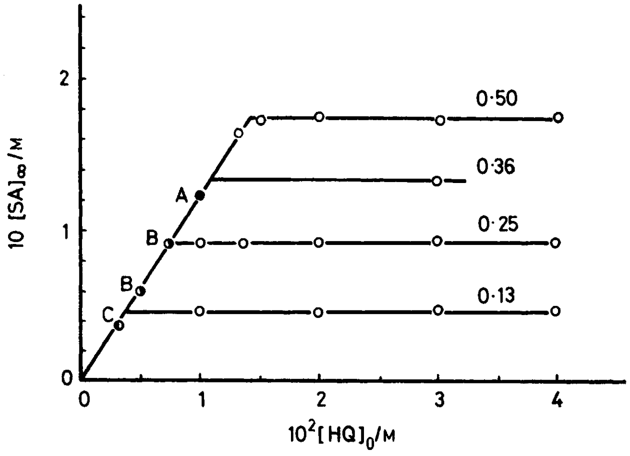

FIGURE 2 Stationary concentration of semiquinone anion $[SA]_\infty$ as a function of initial concentration of hydroquinone, $(HQ)_0$ for different initial MnO_2 weight : liquid volume ratio $[MnO_2]_0$ at 298 K: A 0.36, 0.50; B 0.25, 0.36, 0.50; C 0.13, 0.25, 0.36, 0.50 g l^{-1}

The effects of the initial concentration of hydroquinone

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on the steady concentration of the radical were investigated at various initial MnO_2 ratios at 298 K and the results are shown in Figure 2. The steady concentration of the radical is found to be proportional to the initial hydroquinone concentration up to a certain point depending on the MnO_2 ratio. Above this ratio, the radical concentration is independent of the hydroquinone concentration. Further, this limiting radical concentration is found to be proportional to the initial MnO_2 ratio. Hence, from Figure 2, relations (2) and (3) hold where $[HQ]_0$ and $[MnO_2]_0$ are the

$$[SA]_\infty = b[HQ]_0 : b[HQ]_0 \leqslant c[MnO_2]_0 \qquad (3)$$

$$[SA]_\infty = c[MnO_2]_0 : b[HQ]_0 \geqslant c[MnO_2]_0 \qquad (4)$$

initial concentration of hydroquinone and the MnO_2 weight to liquid volume ratio, respectively, and b and c are constants (b 0.012, c 3.7×10^{-4} mol g^{-1}).

Relations (3) and (4) are derived from the rate equation (5) when $d[SA]/dt = 0$. Here, k is the rate constant. It is

$$d[SA]/dt = k(b[HQ]_0 - [SA])(c[MnO_2]_0 - [SA]) \qquad (5)$$

shown below that the kinetic data obey the rate equation (5). Upon integrating equation (5), except for the case $b[HQ]_0 = c[MnO_2]_0$, equation (6) is obtained. The values

$$\log\left(\frac{b[HQ]_0 - [SA]}{c[MnO_2]_0 - [SA]}\right) = \frac{k}{2.303}(b[HQ]_0 - c[MnO_2]_0)t + \log\left(\frac{b[HQ]_0}{c[MnO_2]_0}\right) \qquad (6)$$

of log $(b[HQ]_0 - [SA]/c[MnO_2]_0 - [SA])$ were plotted against time t at various initial concentrations of hydroquinone and the MnO_2 ratio. The plot of the kinetic data in Figure 1 is shown in Figure 3, and good straight lines were obtained as expected from equation (6). As shown in Figure 4, the slope of the straight lines is proportional to $(b[HQ]_0 - c[MnO_2]_0)$, which also agrees with equation (6). When $b[HQ]_0 = c[MnO_2]_0$, the solution of equation (5) is given as (7). It was confirmed that equation (7) holds

$$(b[HQ]_0 - [SA])^{-1} = (b[HQ]_0)^{-1} + kt \qquad (7)$$

only when $b[HQ]_0 = c[MnO_2]_0$,; a plot of $1/(b[HQ]_0 - [SA])$ *versus* time gave a straight line. Thus, the kinetic results are found to follow equation (5) strictly. The rate constant k is 3.36×10^2 l mol^{-1} min^{-1} at 298 K.

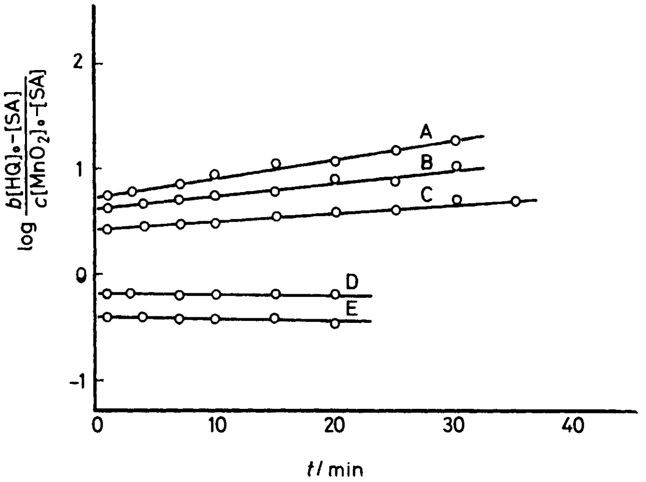

FIGURE 3 log$(b[HQ]_0 - [SA]/c[MnO_2]_0 - [SA])$ against reaction time for different initial concentrations of hydroquinone at 298 K. Initial MnO_2 weight : liquid volume ratio: 0.25 g l^{-1}; $[HQ]_0$ A 40; B 30; C 20; D 5; E 3mM

The dependence of the rate of the radical formation on temperature was investigated for the range 283—313 K. In each case, experiments were carried out with the same initial concentration of hydroquinone and MnO_2 weight to liquid volume ratio. By assuming that the kinetic law (5) is operative throughout the temperature range, the activation energy was determined as 33 ± 2 kJ mol^{-1}, and it was shown that b and c are constant irrespective of the temperature.

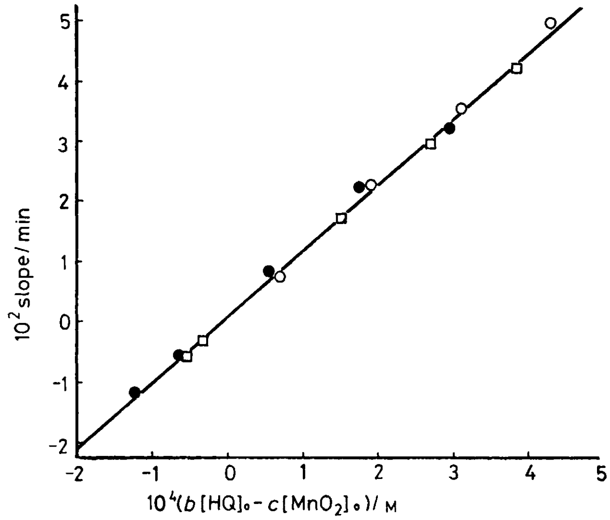

FIGURE 4 Slope of the curve log$(b[HQ]_0 - [SA]/c[MnO_2]_0 - [SA])$ *versus* time is plotted against $b[HQ]_0 - c[MnO_2]_0$. Initial MnO_2 weight : liquid volume ratio: ○ 0.13, □ 0.25, ● 0.50 g l^{-1}

DISCUSSION

In the previous study using a flow technique,[14] the reactions (8) and (9) where SQ denotes neutral semiquinone radical ($\cdot OC_6H_4OH$) were proposed. In step (8), manganese dioxide abstracts a hydrogen atom from a hydroquinone molecule to form a neutral semiquinone radical which desorbs into the liquid phase and is converted into semiquinone anion radical by equilibrium (9) in the pH region studied (9.0). However, the elementary reactions of (8) on the MnO_2 surface have not been elucidated, although it was confirmed that Mn^{IV} on the dioxide surface is reduced to Mn^{II} by the reaction with hydroquinone.[14]

$$HQ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} SQ \qquad \text{on } MnO_2 \text{ surface} \qquad (8)$$

$$SQ \underset{k_4}{\overset{k_3}{\rightleftharpoons}} SA + H^+ \qquad \text{in liquid phase} \qquad (9)$$

Here, we propose the mechanism (10) and (11) for this reaction analogous to that proposed by Pratt *et al.*[7] for the oxidation of diarylmethanes. MnO_2^*, $MnO(OH)^*$,

$$HQ + MnO_2^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SQ + MnO(OH)^* \qquad (10)$$

$$HQ + MnO(OH)^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} SQ + Mn(OH)_2^* \qquad (11)$$

and $Mn(OH)_2^*$ designate the species on the dioxide surface.

From reactions (10) and (11) on the solid surface and (9) in the liquid phase, one obtains the rate equations (12) and (13). Summing equations (12) and (13), one

$$-\frac{d[HQ]}{dt} = \frac{d([SA] + [SQ])}{dt} = k_1[HQ][MnO_2^*] - k_{-1}[SQ][MnO(OH)^*] + k_2[HQ][MnO(OH)^*] - k_{-2}[SQ][Mn(OH)_2^*] \qquad (12)$$

$$\frac{d[MnO(OH)^*]}{dt} = k_1[HQ][MnO_2^*] - k_{-1}[SQ][MnO(OH)^*] - k_2[HQ][MnO(OH)^*] + k_{-2}[SQ][Mn(OH)_2^*] \qquad (13)$$

obtains (14). Here, equilibrium (9) is given in the form

$$\frac{d\{[SA] + [SQ] + [MnO(OH)^*]\}}{dt} = -\frac{1}{2}\frac{d[MnO_2^*]}{dt} = 2k_1[HQ][MnO_2^*] - 2k_{-1}[SQ][MnO(OH)^*] \qquad (14)$$

$$[SQ] = k_4[H^+][SA]/k_3 \qquad (15)$$

(15)[14] where [SA] is much larger than [SQ] since $k_4[H^+]/k_3 \ll 1$ in the pH region studied (9.0). On the supposition that the species $MnO(OH)^*$ is so unstable that hydroquinone reacts with $MnO(OH)^*$ immediately and that relations (16) and (17) hold, equation (14) can

$$k_1[MnO_2^*] = k_2[MnO(OH)^*] \qquad (16)$$

$$[SA] \gg [SQ] + [MnO(OH)^*] \qquad (17)$$

$$\frac{d[SA]}{dt} = 2k_1[HQ][MnO_2^*] - \frac{2k_1k_{-1}k_4[H^+]}{k_2k_3}[SA][MnO_2^*] \qquad (18)$$

be rewritten as (18). $[MnO_2^*]$ is given by equation (19) where α is a constant, equal to the number of surface

$$[MnO_2^*] = \alpha[MnO_2]_0 - [SA]/2 \qquad (19)$$

species MnO_2^* per gram of MnO_2. Then, equation (18) can be further rewritten as (20). The rate equation (20)

$$\frac{d[SA]}{dt} = k_1\left([HQ] - \frac{k_{-1}k_4[H^+]}{k_2k_3}[SA]\right)(2\alpha[MnO_2]_0 - [SA]) \qquad (20)$$

derived from the above mechanism agrees with the experimental equation (6) since $(HQ) \simeq (HQ)_0$.

Comparing equation (20) with (6), the value of α is found to be 1.84×10^{-4} mol (g MnO_2)$^{-1}$. Thus, the number of MnO_2^* species on the dioxide surface is 7.7×10^{18} m^{-2} since the surface area of MnO_2 used is 14.3 m^2 g^{-1}. This value agrees with that obtained by Oei and Garnett[18] for the oxidation of 1,1-diphenyl-2-picrylhydrazine with MnO_2 (10×10^{18} m^{-2}) and by Dollimore *et al.*[11] for the oxidation of cinnamyl alcohol with β-MnO_2 (7.1×10^{18}—14.4×10^{18} m^{-2}). Thus, this study on the formation of semiquinone anion over manganese dioxide leads to a determination of the oxidising capacity of manganese dioxide.

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