Effects of Pressure on the Photoreduction of *p*-Benzoquinone in Normal and Reversed Micellar Systems

Katsuhiro Tamura,* Masatoshi Abe and Masayoshi Terai

Department of Chemical Engineering, Faculty of Engineering, The University of Tokushima, Tokushima 770, Japan

The photoreduction of *p*-benzoquinone (*p*-BQ) in normal and reversed micellar systems has been studied kinetically under high pressures up to 150 MPa. Anionic sodium dodecyl sulphate (SDS) micelles accelerated the reaction, while cationic hexadecyltrimethylammonium bromide (CTAB) micelles retarded it. Pressure promoted the photoreaction in CTAB micellar systems, but not in SDS micelles. The reaction in Aerosol-OT reversed micellar systems (AOT/H₂O/n-heptane) was faster than that in its bulk solvent, n-heptane. Micellar effects were found; however, these occurred at almost the same rates as that in water. The location of *p*-BQ in the micellar systems was studied using data for their critical micelle concentrations. The mechanisms of the reaction are also discussed.

Photochemical reactions in homogeneous systems are little influenced by moderate pressure up to *ca.* 100 MPa, except that the effects of viscosity increase with pressure, which usually retards chemical reactions such as dimerization.¹ On the other hand, large pressure effects are often observed in heterogeneous systems such as micellar solutions, because the properties of micelles (shape, critical micelle concentration,²⁻⁴ solubilization⁵ and aggregation number⁶) are often affected by pressure, and this leads to large pressure effects on the photochemical reactions.^{1,7}

In the present paper we describe the effects of pressure on the photoreduction of p-benzoquinone (p-BQ) in anionic sodium dodecyl sulphate (SDS) micelles, cationic hexadecyltrimethylammonium bromide (CTAB) micelles in aqueous media and di(2-ethylhexyl)sodium sulphosuccinate reversed micelles (AOT/H₂O/n-heptane) at high pressures up to 150 MPa. Micelles in aqueous media solubilize non-polar solutes in the non-polar core or adsorb them on the surfaces and give the reactants organized reaction fields. Reversed micelles provide unique fields to solubilize ionic or polar solutes in apolar media, and can control the reaction rate or pathway occurring in the interior core of the micelles. To check the probability of solubilization of p-BQ in micelles, the solubilities of p-BQ in n-dodecane and n-hexadecane were studied. These alkanes correspond to the hydrocarbons of SDS and CTAB. Furthermore, the effects of p-BQ on the critical micelle concentrations (c.m.c.) of SDS and CTAB were also determined in order to give some indication of the location of the reactants in the micelles.

Experimental

p-Benzoquinone (*p*-BQ) was obtained from Wako and recrystallized twice from ethanol. Sodium dodecyl sulphate (SDS) and hexadecyltrimethylammonium bromide (CTAB) were purchased from Nakarai and washed with diethyl ether for 12 h using a Soxhlet extractor and then recrystallized twice from ethanol. Di(2-ethylhexyl)sodium sulphosuccinate (Aerosol-OT, AOT) (Tokyo Kasei) was dissolved in methanol, filtered, and the solvent was removed under vacuum. n-Dodecane and n-hexadecane were dried with sodium and distilled under reduced pressure. Water was distilled twice, once from potassium permanganate solution.

The apparatus used for the high-pressure experiments consisted mainly of three parts:^{8,9} a high-pressure vessel with quartz windows, a 400 W mercury lamp (Toshiba, H 400-P) and a high-pressure generator (Hikari Kohatsukiki Ltd; KP-3 A). The reaction solution was placed in a sliding cell $(12\phi \times 15 \text{ mm})$, which was convenient as no correction of reactant concentration was required. A silicon photocell (Hamamatsu TV S780-5B) was used to monitor the lamp emission and to correct the concentration of reaction products, since the light intensity might vary with time. A pressure up to 150 MPa was used, and the reaction temperature was controlled at $308 \pm 0.2 \text{ K}$ by circulating water of constant temperature around the high-pressure vessel.

The reaction solution containing 1.00×10^{-3} mol kg⁻¹ *p*-BQ and 1.00×10^{-1} mol kg⁻¹ surfactant was irradiated for the desired time after being pressurized. The residual *p*-BQ was determined by u.v. spectrophotometry, and the apparent first-order rate constants were evaluated. The solubilities of *p*-BQ in n-hexadecane, n-dodecane, n-heptane and water were also determined by u.v. spectrophotometry.

The critical micelle concentrations of SDS and CTAB containing p-BQ were determined by an electric-conductivity method using a Yanagimoto MY-8 conductivity instrument.

Results

The absorption spectra of solutes are strongly dependent on the nature of the media. Accordingly, these spectra provide valuable information on the properties of the environment surrounding the solutes. Table 1 shows the maximum wavelengths (λ_{max}) of *p*-BQ in micellar and non-micellar systems at atmospheric pressure. λ_{max} had two values: 245.7 nm for water and normal micelles in aqueous media and 240.8 nm for n-heptane and reversed micelles (AOT/H₂O/n-heptane). λ_{max} did not depend on the nature of the micelle but on the media used. These results suggest the location of *p*-BQ molecules in micellar systems, namely that *p*-BQ is present in the bulk solvent phase and/or on the surfaces of the micelles and surrounded by the media.

The photoreduction of *p*-BQ was markedly affected by the electric charges of the micelles.¹⁰ The changes in reaction conversion with time in various heterogeneous and homogeneous systems at atmospheric pressure are shown in fig. 1. The results demonstrate large medium effects; for example, SDS aqueous solutions promoted the reaction, while CTAB aqueous solutions retarded it when compared to the water system. Kano and Matsuo indicated the formation of a cationic species as an intermediate of this reaction, based on the concentration effects of micelles,¹⁰ because anionic surfactants accelerated the reaction and cationic surfactants suppressed it. On the other hand, AOT reversed micelles significantly accelerated the reaction as compared to the bulk solvent (n-heptane), and showed almost the same rates as those in water. From these results, the presence of concentration effects from AOT reversed micelles is predictable. A water content up to R = 30 in the interior core of the reversed micelles hardly affect the reaction rates, where R is the molar ratio of water to AOT ($R = [H_2O]/[AOT]$). Water has the ability to promote the photoreduction of *p*-BQ rather than n-heptane.

Table 2 shows the apparent first-order rate constants of the photoreduction of p-BQ in various systems at high pressures up to 150 MPa. The logarithms of the ratios of the rate constants at high and atmospheric pressures (k_p/k_0) plotted against pressure are shown in fig. 2. The pressure dependence of the rate constants are strongly influenced by the nature of the reaction fields, *i.e* normal micellar, reversed micellar and homogeneous systems. The reaction was accelerated by pressure in normal micellar and homogeneous systems but was suppressed in the AOT reversed micellar systems. At a

K. Tamura, M. Abe and M. Terai

Table 1. The maximum wavelengths of p-
benzoquinone in various systems at atmospheric
pressure and 298 K

system	$\lambda_{ m max}/ m nm$
SDS ^a	245.7
water	245.7
$CTAB^{a}$	245.7
n-heptane	240.8
$AOT^a \ (R=2)^b$	240.8
(R=5)	240.8
(R = 20)	240.8
(R = 30)	240.8

^{*a*} [surfactant] = $1.00 \times 10^{-1} \text{ mol kg}^{-1}$. ^{*b*} R = [H₂O]/[AOT].



Fig. 1. Variation with time of the photoreduction conversion of *p*-benzoquinone in micellar and non-micellar systems at atmospheric pressure and 308 K. ①, SDS; ①, water; □ AOT, R = 2; △, AOT, R = 5; ▲, AOT, R = 20; ○, AOT R = 30; ①, n-heptane; ■, CTAB. [surfactant] = 1.00 × 10⁻¹ mol kg⁻¹. [*p*-BQ] = 1.00 × 10⁻³ mol kg⁻¹. R = [H₂O]/[AOT].

water content R = 30 the reaction rates in AOT reversed micelles were greatly reduced at higher pressures. Such drastic changes at $R \approx 30$ were also observed in our studies on the fluorescence polarization of AOT reversed micelles at high pressures.¹¹ These results suggest large fluctuations in the properties of the reaction fields. Zulauf and Eicke studied the effect of temperature on the structures of AOT reversed micelles in iso-octane using photon-correlation spectroscopy.¹² They concluded that polydispersity occurred in these water concentration ranges, with pressure seeming to promote the aggregation of the reversed micelles.

The apparent activation volumes of this reaction (ΔV^{\star}) were estimated using the following equation:

$$\Delta V^{\neq} = -RT(\partial \ln k / \partial p)_{T}$$

where $\ln k$ is the logarithm of the rate constant, and can be shown to be a first-order function of pressure for SDS, water and n-heptane systems, and a second-order function of pressure for CTAB systems. The apparent activation volumes at atmospheric pressure

Photoreduction of p-Benzoquinone in Micelles

	k/10 ⁻⁴ s ⁻¹				
system	0 MPa	30 MPa	50 MPa	100 MPa	150 MPa
SDS ^b	18.3		18.4	20.6	23.9
water	7.5		8.00	8.48	8.98
CTAB ^b	0.725	0.893	0.993	1.06	
n-heptane	1.94	2.03	2.07	2.21	
AOT^{b} $(R = 2)^{c}$	7.47		7.32	6.72	6.93
(R=5)	7.74		7.35	6.98	7.10
(R = 20)	7.45		6.70	6.65	6.37
(R=30)	6.77	6.77	6.57	5.93	

Table 2. Pressure dependence of the apparent first-order rate constant of the photoreduction of p-benzoquinone in micellar and non-micellar systems at 308 K^{α}

^{*a*} [*p*-BQ] = 1.00×10^{-3} mol kg⁻¹. ^{*b*} [surfactant] = 1.00×10^{-1} mol kg⁻¹. ^{*c*} $R = [H_2O]/[AOT]$.



Fig. 2. Plots of $\ln (k_p/k_0)$ vs. p for the photoreduction of p-benzoquinone in micellar and nonmicellar systems at 308 K. \bigcirc , CTAB; \triangle , n-heptane; \bigcirc , SDS; \blacksquare , water; \Box AOT, R = 2; \bigcirc , AOT, R = 5; \blacktriangle , AOT, R = 20; \bigcirc , AOT, R = 30.

are shown in table 3. The activation volumes of the homogeneous systems, water and n-heptane, have small negative values and their absolute values are similar. Such small values are a feature of photochemical reactions in homogeneous systems.⁸ In heterogeneous systems such as SDS or CTAB micellar solutions, large activation volumes can be expected because the micellar structures (shape, size and aggregation number) and the solubilization of reactants are often influenced by pressure, *i.e.* the

K. Tamura, M. Abe and M. Terai

Table 3. Apparent activation volumes of thephotoreduction of p-benzoquinone in micellarand non-micellar systems at atmospheric pressureand 308 K^a

system	$\Delta V^{\neq}/\mathrm{cm}^3 \mathrm{mol}^{-1}$	
SDS	-4.7	
water	-3.0	
СТАВ	-22	
n-heptane	-3.3	
AOT(R = 2)	1.5	
(R=5)	1.7	
(R = 20)	2.4	
(R = 30)	(3.8)	

^{*a*} The concentrations of p-BQ and surfactants are the same as those in table 2.

Table 4. Solubilities of *p*-benzoquinone in various solvents at atmospheric pressure and 308 K

solvents	$[p-BQ]/10^{-2} \text{ mol kg}^{-1}$
n-hexadecane	5.39
n-dodecane	8.83
n-heptane	7.12
water	15.6 ^a

^{*a*} 12.5×10^{-2} mol dm⁻³ [ref. (14)].

 Table 5. Effect of p-benzoquinone on the critical micelle concentration of SDS and CTAB at atmospheric pressure and 308 K

	c.m.c.	
$[p-BQ]/10^{-3} \text{ mol kg}^{-1}$	[SDS]/10 ⁻³ mol dm ⁻³	[CTAB]/10 ⁻⁴ mol dm ⁻³
0	8.10	9.27
	8.07^{a}	9.19 ^a
	8.1 ^b	9.2 ^b
0.5	8.17	9.61
1.0	8.24	9.92
1.5	8.31	10.28
2.0	8.39	10.60

^a At 298 K. ^b At 298 K [(ref. 13)].

properties of the reaction fields change (medium effects). The volume of the CTAB systems had a large negative value $(-22 \text{ cm}^3 \text{ mol}^{-1})$, while that for SDS had a small negative one $(-4.7 \text{ cm}^3 \text{ mol}^{-1})$. In contrast, the apparent activation volumes in AOT reversed micelles had small positive values and increased with increasing water content (*R*) in the interior core $(1.5-3.8 \text{ cm}^3 \text{ mol}^{-1})$.

Table 4 shows the solubilities of p-BQ in n-alkanes (n-heptane, n-dodecane and

1497



Fig. 3. Effect of *p*-benzoquinone on the c.m.c. of SDS (●) and CTAB (○) micellar solutions at atmospheric pressure and 308 K.

n-hexadecane) and water at 308 K. These results show that the micelles of SDS and CTAB can solubilize p-BQ in our concentration ranges, and the AOT reversed micelles also can solubilize p-BQ in both the hydrocarbon phase and the water pool.

The critical micelle concentrations (c.m.c.) of SDS and CTAB containing *p*-BQ were determined by the electric-conductivity method and the values obtained are shown in table 5. To check the correctness of these values, the c.m.c. at 298 K was compared with the values in ref. (13), and good agreement was obtained. The c.m.c. of both surfactants increased linearly with the concentration of *p*-BQ. The ratios of the c.m.c. (c.m.c., $_{p-BQ}$ /c.m.c.₀) are plotted against the concentration of *p*-BQ in fig. 3. The line for CTAB is much steeper than that for SDS.

Discussion

Reaction Mechanisms

Many mechanisms for the photoreduction of p-BQ under different conditions have been proposed. For example, Kurien and Robins¹⁴ showed that the primary photochemical product of aqueous solutions of p-BQ was benzene-1,2,4-triol, and fast reactions followed which produced hydroquinone and 2-hydroxy-1,4-benzoquinone. Joschek and Miller¹⁵ reported that hydroquinone was the only product in oxygen, but that hydroquinone and benzene-1,2,4-triol were obtained as main products in a nitrogen atmosphere. One mechanism proposed for the production of hydroquinone in aqueous media is shown in scheme 1. The semiquinone radical is produced in the first step, and disproportionation of the two radicals creates one hydroquinone molecule. Water is considered to be a hydrogen donor in this reaction because the quantum yield does not change with the concentration of p-BQ.¹⁶ Generally, the ability of hydrogen donors increases in the following order: aliphatic hydrocarbons, alcohols (water) and metal hydrogenates. The slower reduction of p-BQ in n-heptane solution than in water can be

K. Tamura, M. Abe and M. Terai



explained by this order. Although *p*-BQ molecules can be considered as localized in heptane-like environments according to the λ_{max} data for *p*-BQ in AOT reversed micelles (see table 1), the reaction rates in AOT reversed micelles are almost the same as those in water.

An anionic surfactant (SDS) promoted the photoreduction of p-BQ, while cationic CTAB retarded it (see fig. 1). This suggests that a cationic intermediate is formed and



Scheme 2.

is concentrated in the anionic micelles or on the anionic surface of the micelles (concentration effects of micelle). Scheme 2 for the carbonyl group may explain the above results. Thus the cationic properties of the carbonyl group promote the reaction in SDS micellar systems. In contrast, the surface of CTAB micelles are cationic, although some parts are neutralized by the Br^- counter-ions. In this case the electric repulsion between cations prevents the concentration of *p*-BQ molecules in the micelles, and this may be one of the causes of the slow reaction rates. If electric repulsion is the only cause of the slower reaction in CTAB micellar systems, the reaction rates in these systems should be faster than that in water, because *p*-BQ molecules are concentrated in the bulk water phase by the repulsion of *p*-BQ molecules from the CTAB micelles. However, the reaction in CTAB micellar systems is much slower than that in water. The slower reaction in this system is attributed to Br^- ions which generally inhibit the withdrawal of hydrogen radicals from hydrogen donors.

Apparent Activation Volumes

The features of the apparent activation volumes of the *p*-BQ photoreduction are as follows: (1) homogeneous solvents and aqueous micellar solutions have small negative values, (2) the CTAB system only has a large negative value and (3) reversed micelles have small positive values. It is known that the activation volumes for thermal reactions are influenced by the nature of the media.¹⁷ In particular, the reactions in which ions are formed or disappear are strongly affected. However, almost all photoreactions we studied in homogeneous media were hardly influenced by moderate pressures up to ca. 150 MPa, and their apparent activation volumes are very small. Pressure affects micellar properties (c.m.c., solubilization, aggregation number *etc.*), and this often results in large pressure effects on the photoreactions in micellar systems as reaction fields.¹

Nishikido et al. reported that the solubilization of 2-phenylethanol in CTAB micelles

Photoreduction of p-Benzoquinone in Micelles

was enhanced with pressure and had a maximum value at ca. 100 MPa.⁵ It can be seen in fig. 2 that the rate constant of *p*-BQ photoreduction also has a maximum value at ca. 100 MPa. Accordingly, the large pressure effects on the reaction rates (large activation volumes) in CTAB micellar systems may be explained as follows: the solubilization of *p*-BQ increases with pressure up to ca. 100 MPa, and *p*-BQ molecules are concentrated in the micelles. This results in the enhancement of the disproportionation (bimolecular reaction) shown in scheme 1.

Critical Micelle Concentration

Higher alcohols and n-alkanes¹⁸ generally depress the c.m.c., and this is due to the solubilization of these non-electrolytes into the micelle core. In contrast, water-soluble substances such as acetone, ethylene glycol, dioxane or the lower alcohols¹⁸⁻²¹ increase the c.m.c. In these cases additives greatly change the nature of the water phase; therefore, the partition equilibrium of the additives between solvents and micelles and changes in micellar properties become important. These additives depress the dielectric constants of the aqueous solutions and also break the water structure around the hydrocarbons of the surfactants. Both effects should raise the c.m.c.

p-Benzoquinone linearly and effectively increases the c.m.c of CTAB and SDS in its lower concentration range (fig. 3). The concentration ranges of *p*-BQ used in our study are much lower than those of the additives previously described. Therefore, large changes in the nature of the water phase cannot be expected. *p*-Benzoquinone effectively breaks the water structure around the hydrocarbons of the surfactants. CTAB molecules have longer hydrocarbons than SDS, and these differences affect the concentration effects on the increase in c.m.c. Furthermore, three methyl groups on a nitrogen atom promote water structure, so that the effects of *p*-BQ are more significant. A change in the effect of pressure on the c.m.c. with *p*-BQ concentration is not clear; therefore, these c.m.c. data cannot be used to predict the effects of pressure on reaction rates.

References

- 1 K. Tamura and M. Aida, J. Chem. Soc., Faraday Trans. 1, 1986, 82, 1619.
- 2 D. Hamann, J. Phys. Chem., 1962, 66, 1359.
- 3 R. F. Tudden and A. E. Alexander, J. Phys. Chem., 1962, 66, 1839.
- 4 S. Kaneshina, M. Tanaka, T. Tomida and R. Matuura, J. Colloid Interface Sci., 1974, 48, 450.
- 5 N. Nishikido, M. Kishi and M. Tanaka, J. Colloid Interface Sci., 1983, 94, 348.
- 6 N. Nishikido, M. Shinozaki, G. Sugihara, M. Tanaka and S. Kaneshina, J. Colloid Interface Sci., 1980, 74, 474.
- 7 K. Tamura and M. Suminaka, J. Chem. Soc., Faraday Trans. 1, 1985, 81, 2287.
- 8 K. Tamura and S. Sugiyama, Bull. Fac. Eng. Univ. Tokushima, 1984, 21, 33.
- 9 K. Tamura and S. Sugiyama and W. J. le Noble, J. Org. Chem., 1984, 49, 3836.
- 10 K. Kano and T. Matsuo, Chem. Lett., 1973, 1127.
- 11 K. Tamura and N. Nii, J. Phys. Chem., in press.
- 12 M. Zulauf and H. F. Eicke, J. Phys. Chem., 1979, 83, 480.
- 13 J. H. Fendler and E. J. Fendler, Catalysis in Micellar and Macromolecular Systems (Academic Press, New York, 1975), p. 20.
- 14 K. C. Kurien and P. A. Robins, J. Chem. Soc. B, 1970, 855.
- 15 H. I. Joschek and S. J. Miller, J. Am. Chem. Soc., 1966, 88, 3273.
- 16 S. Hashimoto, K. Kano and H. Okamato, Bull. Chem. Soc. Jpn, 1972, 45, 966.
- 17 K. E. Weale, Chemical Reactions at High Pressures (Spon, London, 1967), p. 137.
- 18 W. D. Harkins, R. Mittelman and M. L. Corrin, J. Phys. Colloid Chem., 1949, 53, 1350.
- 19 B. D. Flockhart, J. Colloid Sci., 1957, 12, 557.
- 20 K. Shirahama and R. Matuura, Bull. Chem. Soc. Jpn, 1965, 38, 373.
- 21 A. W. Ralston and D. N. Eggenberger, J. Phys. Colloid Chem., 1948, 52, 1494.

Paper 8/03056A; Received 28th September, 1988