

Surface-Active Properties and Their Photochemical Behaviors of (1-Alkyl-4-pyridiniummethyl)phosphonates

Yoshiki OKAMOTO,* Asao HOSODA, and Setsuo TAKAMUKU

The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka, Ibaraki, Osaka 567

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Synopsis. (1-Alkyl-4-pyridiniummethyl)phosphonates bearing long alkyl-chains of even carbon numbers of 8 to 18 were prepared. They exhibited the characteristics of surface-active agents. Upon irradiation in alkaline aqueous media, the phosphonates underwent the C-P bond cleavage to give 1-alkyl-4-methylpyridinium phosphates and as a result the surface tension of the solution also changed. The two-fold increases of the quantum yields of the C-P bond cleavage were found at their critical micelle concentrations.

Upon UV-irradiation in alkaline aqueous media, (*p*-nitrobenzyl)-¹⁾ or (*p*-benzoylbenzyl)phosphonic acid²⁾ underwent C-P bond cleavage to give *p*-nitrotoluene or 4-methylbenzophenone and orthophosphate, respectively. [4-(4-Alkoxybenzoyl)benzyl]phosphonic acid bearing a long alkyl chain, which had the characteristic of an anionic surface-active agent, also underwent the C-P bond cleavage to loss the characteristics.^{2b)}

On the other hand, recently, we have reported that upon UV-irradiation under the same conditions (1-benzylpyridiniummethyl)phosphonates also underwent C-P bond cleavage to give 1-benzylpyridinium phosphate in an almost quantitative yield.^{3b)}

In this paper, we report the surface active properties and the photochemical behaviors of (1-alkyl-4-pyridiniummethyl)phosphonates (**1a**–**f**) bearing long alkyl chains, which must be expected to act as amphoteric surface active agents.

Results and Discussion

(1-Alkyl-4-pyridiniummethyl)phosphonates (**1a**–**f**) bearing long alkyl chains of even carbon numbers of 8 to 18 were prepared by the analogous method as described previously.³⁾ The acids, **1a** and **1b**, bearing the comparatively shorter alkyl chains (carbon number of 8 and 10) were well soluble in aqueous solution at ambient temperature, but solubilities of **1c**–**f** bearing the longer alkyl chains (even carbon numbers of 12–18) were not enough to secure a sufficiently well-characteristics. However, in alkaline media, all the phosphonates were well dissolved in water. The surface tensions of the aqueous solutions of **1a**–**f** (1.0 – 30×10^{-3} mol dm⁻³, pH 11, 21 °C) were determined by using a Du Nouy surface tensiometer. The relationships between the surface tension and the concentration of the solutions are shown in Fig. 1.

All surface tensions of the aqueous solutions of **1b**–**f** were reduced to about 53 dyn cm⁻¹ (21 °C) by the increase of the concentration (1 dyn=10⁻⁵ N). The surface active property of **1a** was inferior to others. The critical micelle concentrations (CMC) were

observed in the range of 2.0×10^{-3} to 2.0×10^{-2} mol dm⁻³, and the CMC were lowered by the increase of their alkyl-chain lengths.

The change of the surface tension of the solution by temperature was no less larger than that of water itself.

The effect of pH on the surface tension of **1d** (5.0×10^{-3} mol dm⁻³, 21 °C) is shown in Fig. 2. The surface tension of an acidic solution was lower compared to that of an alkaline solution.

We have reported that upon UV-irradiation in alkaline aqueous media (1-benzyl-4-pyridiniummethyl)phosphonate underwent C-P bond cleavage via intramolecular electron transfer to give 1-benzyl-4-methylpyridinium phosphate in an almost quantita-

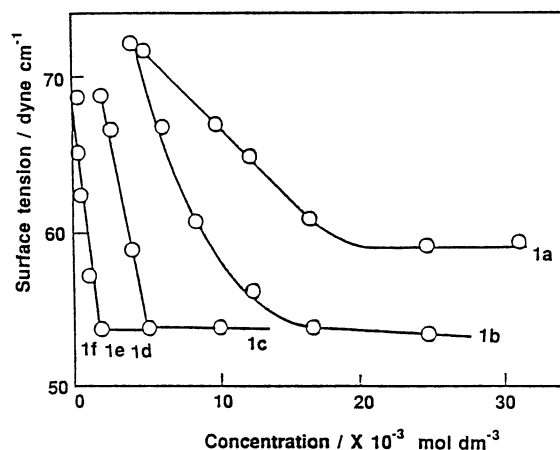


Fig. 1. The relationship between surface tension and the concentration of **1a**–**f** in aqueous solution (21 °C, pH 11).

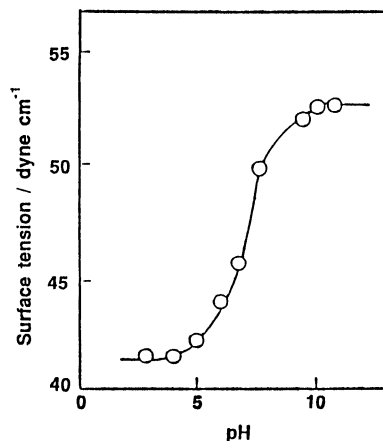
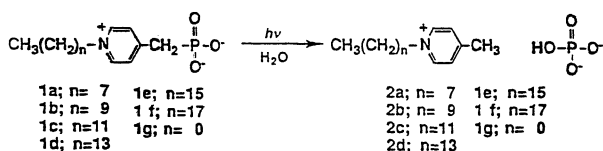


Fig. 2. The effect of pH on surface tension of the aqueous solution of **1d** (5.0×10^{-3} mol dm⁻³, at 21 °C).



Scheme 1.

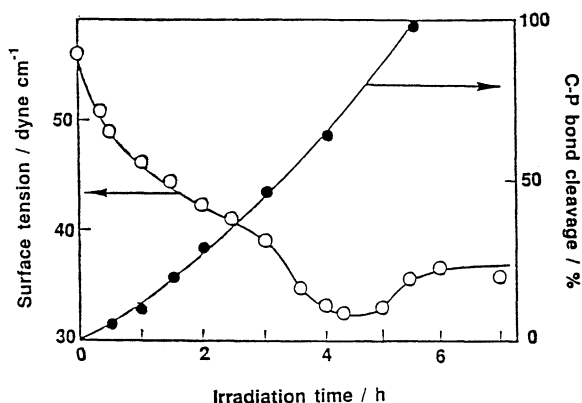


Fig. 3. The change of surface tension of the aqueous solution and the percentage of C-P bond cleavage of **1d** as a function of irradiation time (5.0×10^{-3} mol dm $^{-3}$, at 21 °C, pH 11).

tive yield (quantum yield 0.04).^{3b,4)} Under the same conditions, the acids **1a–f** also underwent C-P bond cleavage to give the corresponding 1-alkyl-4-methylpyridinium phosphates (**2a–f**) in quantitative yields, which were determined by the comparison of ^1H and ^{31}P NMR data with those of the authentic samples (Scheme 1).

The change of surface tension of the solution of **1d** (5.0×10^{-3} mol dm $^{-3}$, 21 °C, pH 11) and the yield of orthophosphate as a function of irradiation time (h) are shown in Fig. 3.

Upon irradiation, the surface tension was reduced gradually until that of 1-tetradecyl-4-methylpyridinium phosphate (**2d**, 37 dyn dm $^{-3}$, 5.0×10^{-3} mol dm $^{-3}$, pH 7.5) which was prepared by other method, because the photolyzed product **2d** also exhibited the characteristic of a cationic surface active agent itself, which was superior to that of **1d**. A depression was observed in the midst of the curve, but the reason can not be made clear. The pH of the solution was also gradu-

ally reduced from 11 to 7.5 presumably due to formation of orthophosphate.

The quantum yields of orthophosphate at several concentrations are given in Table 1.

In all the case, two-fold increases in the quantum yields for the C-P bond cleavage were observed in micelle concentrations compared to more dilute aqueous solutions.

In the case of (1-methyl-4-pyridiniummethyl)phosphonic acid (**1g**), which did not form a micelle, the quantum yield for production of orthophosphate did not change by the increase of the concentration. Their yields were constant over the all range of 5.0×10^{-4} to 2.0×10^{-2} mol dm $^{-3}$ within an experimental error as shown in Table 1.

During the past decade aqueous micellar solutions have been extensively used as media for photochemical reactions and have been found in many situations to dramatically change the nature and/or rate of a reaction compared to homogeneous media.

In general, there are five common types of effects that micelles can produce on reactions: cage, local concentration, viscosity, polarity, and electrostatic effects.⁵⁾

This change of the quantum yield of C-P bond cleavage at the CMC may be explained by micelle aggregates. In the solution above CMC, the orientation of the molecules within the Stern layer may be well-suited for intra- or intermolecular electron transfer. But the facts that an intermolecular electron transfer takes place has not been found yet in this system.

Several other proton and electron transfer reactions have been also studied in micellar systems.⁵⁾

Experimental

Mps or dps were obtained with a Yanagimoto Micro Melting Point Apparatus and uncorrected. UV-visible spectra were recorded with a Hitachi 150-20 spectrometer with MeOH as solvent. ^1H NMR spectra were determined on a solution in D $_2$ O with sodium 3-trimethylsilyl-1-propanesulfonate (DSS) as an internal standard on a Bruker-AM360 spectrometer. ^{31}P NMR spectra were determined on a solution in H $_2$ O/D $_2$ O with 80% H $_3$ PO $_4$ as an external standard on a JNM FX90P.

Preparation of (1-Alkyl-4-pyridylmethyl)phosphonates (1a–f). General Procedure: A mixture of (4-pyridyl-

Table 1. Effects of Alkyl-Chain Length and Formation of Micelle on the Quantum Yields^{a)}

Compounds	CMC	Quantum yield (×10)						ϕ_M/ϕ_0 ^{b)}
	×10 ^{−3} mol dm ^{−3}	Concn/×10 ^{−3} mol dm ^{−3}						
		0.5	1.0	2.0	5.0	10	20	
1a	19	—	—	—	0.40	0.43	0.86	2.1
1b	11	—	—	—	0.41	0.42	0.88	2.1
1c	4.5	—	—	0.46	0.89	0.87	—	2.1
1d	2.1	—	0.45	0.47	1.02	0.97	—	2.2
1e	2.0	—	0.46	0.98	0.93	0.95	—	2.1
1f	1.9	0.43	0.41	0.89	0.86	0.87	—	2.1
1g	—	0.41	0.42	0.39	0.40	0.41	0.38	—

a) Aqueous solution, at 21 °C, pH 11. b) The ratio of the quantum yields in micelle (ϕ_M) and in dilute solution (ϕ_0).

methyl)phosphonate (6.9 g, 30 mmol) and alkyl iodide (33 mmol) in acetonitrile (50 ml) was stirred at ambient temperature. The reaction was complete after an overnight stirring (monitored by ^1H NMR spectrometry), and then lithium bromide (5.7 g, 66 mmol) and trimethylsilyl chloride (7.2 g, 66 mmol) were added to the mixture. The mixture was refluxed for 4 h. After the precipitated lithium chloride was filtered, the solvent and ethyl bromide were distilled off by means of an aspirator. The residue was hydrolyzed with water. The crude product was purified by recrystallization from ethanol.

(1-Octyl-4-pyridiniumethyl)phosphonate (1a): Mp 147–149 °C; $UV_{\max}$ (MeOH) 245 nm (ϵ 13100); $\delta=0.86$ (3H, t, $J_{\text{HH}}=7.0$ Hz), 1.29 (10H, m), 2.00 (2H, m), 3.41 (2H, d, $J_{\text{HP}}=21.11$ Hz), 4.56 (2H, t), 7.91–8.68 (4H, m); Found: C, 58.58; H, 8.71; N, 4.49%. Calcd for $\text{C}_{14}\text{H}_{24}\text{NO}_3\text{P}$: C, 58.93; H, 8.48; N, 4.91%.

(1-Dodecyl-4-pyridiniumethyl)phosphonate (1b): Mp 150–151 °C; $UV_{\max}$ (MeOH) 245 nm (ϵ 12800); $\delta=0.83$ (3H, t, $J_{\text{HH}}=7.0$ Hz), 1.26 (12H, m), 2.08 (2H, m), 3.48 (2H, d, $J_{\text{HP}}=21.1$ Hz), 4.68 (2H, t), 8.06–8.80 (4H, m); Found: C, 60.95; H, 9.09; N, 4.39%. Calcd for $\text{C}_{16}\text{H}_{28}\text{NO}_3\text{P}$: C, 61.32; H, 9.01; N, 4.46%.

(1-Dodecyl-4-pyridiniumethyl)phosphonate (1c): Mp 156–157 °C; $UV_{\max}$ (MeOH) 245 nm (ϵ 13700); $\delta=0.84$ (3H, t, $J_{\text{HH}}=7.0$ Hz), 1.26 (18H, m), 2.00 (2H, m), 4.58 (2H, t), 7.95–8.61 (4H, m); Found: C, 63.59; H, 9.49; N, 4.43%. Calcd for $\text{C}_{18}\text{H}_{32}\text{NO}_3\text{P}$: C, 63.32; H, 9.45; N, 4.10%.

(1-Tetradecyl-4-pyridiniumethyl)phosphonate (1d): Mp 155–157 °C; $UV_{\max}$ (MeOH) 245 nm (ϵ 13600); $\delta=0.83$ (3H, t, $J_{\text{HH}}=7.0$ Hz), 1.21 (22H, m), 2.00 (2H, m), 4.55 (2H, t), 7.92–8.65 (26H, m); Found: C, 64.92; H, 9.74; N, 3.78%. Calcd for $\text{C}_{20}\text{H}_{36}\text{NO}_3\text{P}$: C, 65.01; H, 9.82; N, 3.79%.

(1-Hexadecyl-4-pyridiniumethyl)phosphonate (1e): Mp 150–152 °C; $UV_{\max}$ (MeOH) 245 nm (ϵ 14100); $\delta=0.83$ (3H, t, $J_{\text{HH}}=7.0$ Hz), 1.27 (26H, m), 2.00 (2H, m), 4.61 (2H, t), 7.95 (2H, m); Found: C, 65.13; H, 10.05; N, 3.41%. Calcd for $\text{C}_{22}\text{H}_{40}\text{NO}_3\text{P}$: C, 66.47; H, 10.14; N, 3.52%.

(1-Octadecyl-4-pyridiniumethyl)phosphonate (1f): Mp 152–154 °C; $UV_{\max}$ (MeOH) 245 nm (ϵ 11100); $\delta=0.83$ (3H, t, $J_{\text{HH}}=7.0$ Hz), 1.27 (30H, m), 2.00 (2H, m), 4.61 (2H, t), 7.95 (2H, m); Found: C, 67.21; H, 9.96; N, 3.04%. Calcd for $\text{C}_{24}\text{H}_{44}\text{NO}_3\text{P}$: C, 67.73; H, 10.42; N, 3.29%.

(1-Methyl-4-pyridiniumethyl)phosphonate (1g): The crude product was purified with HPLC using Dowex 1 $\times$ 4 (200–400 mesh, OH form). Aqueous acetic acid (0.1 M) was used as an eluent. A pure product was obtained by recrystallization from water. Mp 232–233 °C (decomp); $UV_{\max}$ (H_2O) 256 nm (ϵ 15000); $\delta=3.42$ (2H, d, $J_{\text{HP}}=22$ Hz), 4.25 (3H, s), 7.84 (2H, d, $J_{\text{HH}}=6.0$ Hz), 8.5 (2H, d); Found: C, 45.01; H, 5.42; N, 7.53%. Calcd for $\text{C}_7\text{H}_{10}\text{NO}_3\text{P}$: C, 44.93; H, 5.39; N, 7.49%.

Measurement of Surface Tension of the Aqueous Solutions of 1. A 20 ml of aqueous solution of prescribed concentration of **1**, whose pH was adjusted with sodium hydroxide, was placed in a beaker (diameter 100 mm) and then the surface tension was measured by a Du Nouy surface tensiometer (Shimadzu) at 21 °C.

Products Analysis (Typical Procedure). A 3-ml aqueous

solution of **1d** (1.0×10^{-2} mol dm $^{-3}$, pH was adjusted with 1 M NaOH aqueous solution) was placed in a quartz tube ($\phi=10$ mm) and purged of dissolved air by bubbling with argon gas. It was irradiated with a merry-go-round apparatus using a high-pressure mercury lamp (300W) at ambient temperature for 8 h. After irradiation the mixture was acidified with HCl aqueous solution, and the water was evaporated in vacuo. The residue was analyzed by ^1H and ^{31}P NMR spectrometry by comparison with the data of an authentic sample which was commercially available.

The product **2d** [^1H NMR (D_2O , DSS) $\delta=0.88$ (3H, $J_{\text{HH}}=7.0$), 1.1–1.6 (22H, m), 1.9–2.2 (2H, m), 2.75 (3H, s), 4.91 (2H, t, $J_{\text{HH}}=6.0$ Hz), 7.9–9.4 (4H, m), ^{31}P NMR ($\text{H}_2\text{O}/\text{D}_2\text{O}$, 80% H_3PO_4) $\delta=2.53$ (s)] was obtained in yields of 92%.

Irradiation and Measurement of the Surface Tension and the Yields of Orthophosphate. A 20 ml of aqueous solution of **1** was placed in a beaker (diameter 100 mm), and a apparatus designed using light from a 1-kW super-high-pressure mercury lamp focused by an aluminum parabolic mirror into a 100 mm beam was used for irradiation. The solution was irradiated over the surface. After irradiation of desired period, the surface tension and the yield of orthophosphate of the solution produced were determined.

Measurement of the Quantum Yield. The quantum yield was on the basis of generated orthophosphate. A 3-ml aqueous solution of **1** (1.0×10^{-2} mol dm $^{-3}$) in a quartz cell (10 mm $\times$ 10 mm) was irradiated. A low-pressure mercury lamp (60 W) with a Vycor glass filter was used as a 254-nm radiation source in the same manner described previously.³⁾

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