# Two-Phase Stopped-Flow Measurement of the Protonation of Tetraphenylporphyrin at the Liquid–Liquid Interface

## Hirohisa Nagatani and Hitoshi Watarai\*

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

The formation rate of the protonated form of tetraphenylporphyrin (TPP) in a dispersed two-phase system composed of dodecane and aqueous trichloroacetic acid (TCA) was studied by means of a stopped-flow method. The protonation reaction took place at the liquid-liquid interface, and the diprotonated TPP (H<sub>2</sub>TPP<sup>2+</sup>) formed was adsorbed there. In order to determine the ratedetermining process, changes in absorbance at the absorption maximum wavelengths of TPP and H<sub>2</sub>TPP<sup>2+</sup> were analyzed. The obtained rate constant for the decrease of TPP in the organic phase,  $21 \pm 2 \text{ s}^{-1}$ , was in agreement with that for the increase of diprotonated TPP at the interface, 20  $\pm$  3 s<sup>-1</sup>. The observed rate constants did not show any dependence on concentrations of both TPP and the acid. The experimental results suggested the ratedetermining step to be the molecular diffusion process of TPP in the stagnant layer in the organic phase side at the liquid-liquid interface, and the thickness of the stagnant layer was estimated as  $1.4 \times 10^{-4}$  cm.

The kinetic mechanism of solvent extraction includes, in general, bulk phase reactions and interfacial reactions. The bulk phase reactions, e.g., acid-base reactions and metal complexation reactions in aqueous phases, have been studied extensively by applying various kinetic methods.<sup>1</sup> The interfacial reactions, however, have been less understood in comparison with the bulk phase reactions.

Recently, the role of interfacial reaction in metal extraction kinetics was demonstrated by means of the high-speed stirring method, employing various extraction systems including chelate extraction, ion-association extraction, and synergic extraction.<sup>2,3</sup> It has been shown in the previous studies, for example, that the ion-association extraction rate of Fe(II) with a hydrophobic 1,10-phenanthroline is governed by the formation rate of the 1:1 complex at the liquid–liquid interface,<sup>4</sup> while the ion-association extraction rate of tetrabutylammonium picrate is controlled by the diffusional mass transfer rate rather than the ion-pairing chemical reaction itself.<sup>5</sup> Now, it is highly necessary to find any kinetic criteria to distinguish between a mass transfer regime and a chemical reaction regime.

(5) Cantwell, F. F.; Freiser, H. Anal. Chem. 1988, 60, 226-230.

The stopped-flow method has been widely employed for kinetic studies in homogeneous, micellar,<sup>6</sup> and microemulsion systems,<sup>7</sup> but it has rarely been applied to the study of reaction mechanisms in liquid—liquid two-phase systems in relevance to the solvent extraction. This method has, however, potential capabilities to produce a dispersed two-phase system by mixing rapidly an aqueous solution with an organic solution, and then to detect the rapid reactions in the dispersed system, which may attain equilibria within a few hundred milliseconds. Furthermore, the reaction at the liquid—liquid interface must be measured directly by two-phase stopped-flow spectrophotometry, provided that the reaction is accompanied by a sufficient spectral change for the detection.

Tetraphenylporphyrin (TPP) is a highly hydrophobic chelate reagent with a very large molar absorbtivity, e.g.,  $4.33 \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> at 416.0 nm in dodecane; hence, it has a bright prospect for use as an extraction–spectrophotometric reagent. TPP is known to be protonated by the attack of hydroen ions<sup>8.9</sup> and to produce the diprotonated species (H<sub>2</sub>TPP<sup>2+</sup>), which is sparingly soluble in water.

$$TPP + 2H^+ \rightarrow H_2 TPP^{2+}$$
(1)

When an organic solution containing TPP and an aqueous acid solution are put into contact, the protonation reaction takes place at the liquid–liquid interface, and the diprotonated TPP is adsorbed there.<sup>10</sup> The heterogeneous reaction will proceed through two steps: (1) the molecular diffusion process of TPP from the organic phase and hydrogen ions from the aqueous phase to the liquid–liquid interface and (2) the chemical reaction between TPP and hydrogen ions at the interface. In this case, it is not necessary to consider the distribution of TPP into an aqueous phase, since TPP is not soluble in water. The protonation is accompanied by the distinctive spectral shift at the Soret band from 416.0 (TPP) to 438.0 nm (H<sub>2</sub>TPP<sup>2+</sup>). The large molar absorbtivity of TPP and the large spectral shift in the protonation are thought to be well suited for an in situ spectrophotometric study of the protonation reaction at the liquid–liquid interface.

In this work, the kinetics of the formation of the diprotonated TPP in the dispersed dodecane—aqueous acid system was studied

- (9) Hibbert, F.; Hunte, P. P. K. J. Chem. Soc. Perkin Trans. 2 1977, 1624-
- (10) Watarai, H.; Chida, Y. Anal. Sci. **1994**, 10, 105–107.

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Amdur, I.; Hammes, G. G. *Chemical Kinetics*, McGraw-Hill, Inc.: New York, 1966; Chapters 5 and 6.

<sup>(2)</sup> Watarai, H. Trends Anal. Chem. 1993, 12, 313-318.

<sup>(3)</sup> Freiser, H. Bull. Chem. Soc. Jpn. 1988, 61, 39-45.

<sup>(4)</sup> Watarai, H.; Sasaki, K.; Sasaki, N. Bull. Chem. Soc. Jpn. **1990**, 63, 2797–2802.

<sup>(6)</sup> Robinson, B. H.; White, N. C.; Mateo, C. Adv. Mol. Relax. Processes 1975, 7, 321–338.

<sup>(7)</sup> Fletcher, P. D.; Howe, A. M.; Robinson, B. H. J. Chem. Soc. Faraday Trans. 1 1987, 83, 985–1006.

<sup>(8)</sup> Hibbert, F.; Hunte, P. P. K. J. Chem. Soc. Chem. Commun. 1975, 728-729.

by means of two-phase stopped-flow spectrophotometry, in order to clarify the rate-determining step in the interfacial protonation.

## **EXPERIMENTAL SECTION**

**Reagents.** *meso*- $\alpha$ , $\beta$ , $\gamma$ , $\delta$ -Tetraphenylporphyrin was obtained from Dojindo Laboratories (Kumamoto, Japan) and dissolved in dodecane at concentrations ranging from 1.48 imes 10<sup>-6</sup> to 3.78 imes10<sup>-5</sup> mol dm<sup>-3</sup>. Dodecane, G.R., used as an organic solvent, was purchased from Nakarai Tesque (Kyoto, Japan) and was highly purified by distilling after treatment with a mixture of fuming sulfuric acid and sulfuric acid. Trichloroacetic acid (TCA), G.R., from Nakarai Tesque, was diluted at concentrations from 1.0  $\times$  $10^{-3}$  to 0.10 mol dm<sup>-3</sup>. The ionic strength of TCA solutions was maintained at 0.10 by the addition of trichloroacetic acid sodium salt, because the dispersion state of the mixture may be influenced by the ionic strength of the aqueous solution. In this condition, the dissociation constant of TCA,  $pK_a$ , is 0.66.<sup>11</sup> Therefore, the concentration of the hydrogen ion in aqueous solution was calculated from this value and the total concentration of TCA. The aqueous solutions were prepared with water distilled and deionized through a Milli-Q system (Millipore, Milli-Q SP.TOC.).

**Apparatus.** A conventional stopped-flow spectrophotometer (Unisoku, RSP-601) was used to measure the protonation reaction in the dispersed systems. The optical cell used for the stopped-flow measurements was a cylindrical quartz cell of 2.0 min i.d. (i.e., 2.0 mm maximum optical path length) and 6.0 mm o.d. and was thermostated at 298.2  $\pm$  0.1 K. A photodiode array UV– visible detector was used to observe the change in the absorption spectrum. The radii of the dispersed droplets were measured by an optical microscope (Nikon, Labphot YF) installed with a CCD video system. In the present experiment, the dodecane phase was the continuous phase and the aqueous phase was the disperse phase. The averaged radius of the dispersed aqueous droplets,  $r_0$ , was estimated as  $(3.3 \pm 0.9) \times 10^{-3}$  cm from the video pictures.

Kinetic Measurements. A dodecane solution containing TPP and an aqueous solution containing TCA in a couple of gas-drive syringes were mixed in a volume ratio of 1:1 by a two-jet mixer. The total volume of the mixture was 0.2 mL for each kinetic run. The dispersed droplet system of dodecane and aqueous phase was so rapidly produced in the optical cell that it was sufficiently agitated for more than  $\sim$ 1000 ms by the initial mixing energy without using any surfactant. After a long time standing, the droplets gradually coaggurated and finally separated into two phases. The progress of the protonation reaction at the liquidliquid interface was followed by acquiring the absorption spectra from 346.0 to 554.0 nm at 5.0 ms intervals. The apparent firstorder rate constants for the decrease of TPP and the increase of diprotonated TPP were obtained by analyzing the absorbance changes at each absorption maximum wavelength. A series of experiments to examine the dependence of the apparent reaction rate constants on the TPP and TCA concentrations was carried out by using 1.0  $\times$  10^{-2} mol dm^{-3} TCA solution and 1.90  $\times$  10^{-5} mol dm<sup>-3</sup> TPP solution, respectively.

Beer's law was examined in the dispersed two-phase system produced by mixing TPP in dodecane with 0.10 mol dm<sup>-3</sup> sodium trichloroacetate solution or  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> TCA solution. A linear relationship was obtained between the TPP absorbance and the TPP concentrations from  $1.48 \times 10^{-6}$  to  $3.78 \times 10^{-5}$  mol dm<sup>-3</sup>.



**Figure 1.** Logarithmic plot of  $[H_2TPP^{2+}]_i S/[TPP]_o V_o$  versus the concentration of hydrogen ion in an aqueous phase. The concentration of TPP used in this experiment was  $7.62 \times 10^{-6}$  mol dm<sup>-3</sup>, and the total concentration of trichloroacetate was 0.10 mol dm<sup>-3</sup>.

Thus, Beer's law was confirmed, and the molar absorbtivities for TPP and the diprotonated TPP in the dispersed two-phase system were determined as  $5.85 \times 10^5$  and  $5.71 \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, respectively.

The protonation of TPP at the dodecane-water interface is written as

$$TPP_{o} + 2H^{+} \rightleftharpoons H_{2}TPP_{i}^{2+}$$
(2)

where the subscripts o and i denote the bulk dodecane phase and the interface, respectively. The diprotonated TPP is expected to adsorb at the interface, forming an ion-pair with the anion, i.e., trichloroacetate ion (TCA<sup>-</sup>), in the present system. The protonation equilibrium was reached at  $\sim$ 500 ms. The equilibrium constant,  $K_{\rm e}$ , for eq 2 can be defined by

$$K_{\rm e} = \frac{[{\rm H}_2 {\rm TPP}^{2^+}]_{\rm i} S_{\rm i} / V_{\rm o}}{[{\rm TPP}]_{\rm o} [{\rm H}^+]^2}$$
(3)

where [TPP]<sub>o</sub> (mol dm<sup>-3</sup>) and [H<sub>2</sub>TPP<sup>2+</sup>]<sub>i</sub> (mol dm<sup>-2</sup>) are the bulk concentration of TPP in a dodecane phase and the interfacial concentration of the diprotonated TPP at the equilibrium state, respectively, *S*<sub>i</sub> is the total area of the dodecane—water interface, and *V*<sub>o</sub> is the volume of the dodecane phase. The values of [H<sub>2</sub>-TPP<sup>2+</sup>]<sub>i</sub>*S*<sub>i</sub>/[TPP]<sub>o</sub>*V*<sub>o</sub> could be calculated from the absorbances of both species at 1000.0 ms and the molar absorbtivities. The obtained values of the concentration ratio were plotted in Figure 1 as a function of the hydrogen ion concentration. The slope of the linear plot was 1.9, as expected from eq 2, confirming the formation of the diprotonated TPP. From the intercept, the value of the equilibrium constant was obtained as 8 × 10<sup>4</sup> mol<sup>-2</sup> dm<sup>6</sup>. This value is larger than the 7.7 × 10<sup>3</sup> mol<sup>-2</sup> dm<sup>6</sup> determined in a DMSO-H<sub>2</sub>O mixture,<sup>9</sup> suggesting preferential stabilization of the diprotonated TPP at the dodecane—water interface.

#### **RESULTS AND DISCUSSION**

The spectral change in Figure 2 shows the decrease of TPP in the dodecane phase and the increase of the diprotonated TPP at the liquid–liquid interface after the mixing. In order to

<sup>(11)</sup> Martell, A. E.; Smith, R. M. Critical Stability Constants, Vol. 3; Plenum Press: New York, 1977; p 19.



Figure 2. Typical spectral change of the dispersed two-phase

system made by rapid mixing of TPP dodecane solution with TCA aqueous solution, measured at 50.0 ms intervals. The concentrations of TPP and TCA were  $1.90 \times 10^{-5}$  and  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>, respectively. The total concentration of trichloroacetate was 0.10 mol dm<sup>-3</sup>.



**Figure 3.** First-order kinetic profiles at the absorption maximum wavelengths,  $\lambda_{max} = 416.0$  nm for TPP and 438.0 nm for H<sub>2</sub>TPP<sup>2+</sup>. Solid lines are the fitting curves obtained by the first-order analysis.

determine the increasing rate constants of the diprotonated TPP, changes in absorbance at the absorption maximum wavelengths ( $\lambda_{max}$ ), 416.0 nm for TPP and 438.0 nm for the diprotonated TPP, were analyzed. Figure 3 shows the changes in absorbance at each  $\lambda_{max}$  after subtraction of the base line drift. The absorbance changes obeyed pseudo-first-order kinetics, since the concentration of hydrogen ion in the aqueous phase was in large excess. The rate law can be written as

$$-\frac{\mathrm{d}[\mathrm{TPP}]_{\mathrm{o}}}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{H}_{2}\mathrm{TPP}^{2+}]_{\mathrm{i}}}{\mathrm{d}t}\frac{S_{\mathrm{i}}}{V_{\mathrm{o}}} = k[\mathrm{TPP}]_{\mathrm{o}} \qquad (4)$$

where k (s<sup>-1</sup>) is the observed rate constant.

The values of the rate constant were evaluated by a curvefitting of the absorbance data from 4.0 to 154.0 ms. The observed rate constants for the decrease of TPP and for the increase of the diprotonated TPP under the various concentrations of TPP or hydrogen ion are summarized in Table 1. The results show that the *k* values depended on neither concentration of TPP nor hydrogen ion. From the experiments varying the concentration of hydrogen ion, the averaged values of rate constants were  $21 \pm 2 \text{ s}^{-1}$  for the consumption of TPP and  $20 \pm 3 \text{ s}^{-1}$  for the formation

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Table 1. Dependence of the Observed Rate Constants<sup>a</sup> on the Concentrations of TPP and Hydrogen Ion at 298 K

dependence on concn of TPP <sup>b</sup>			dependence on concn of hydrogen ion <sup>c</sup>		
[TPP]/	rate constant <sup>d</sup>		[H <sup>+</sup> ]/	rate constant <sup>d</sup>	
mol dm <sup>-3</sup>	$k_{\rm d}/{\rm s}^{-1}$	$k_{\rm i}/{ m s}^{-1}$	mol dm <sup>-3</sup>	$k_{\rm d}/{\rm s}^{-1}$	$k_{\rm i}/{ m s}^{-1}$
$1.5  \times  10^{-6}$	$14.2\pm2.4$	$23.6\pm4.1$	$2.0 \times 10^{-3}$	$20.9 \pm 6.6$	$19.2\pm3.3$
$2.2 imes10^{-6}$	$20.1\pm7.8$	$14.3\pm3.5$	$3.0  imes 10^{-3}$	$25.0\pm5.2$	$22.9\pm0.2$
$2.9 imes10^{-6}$	$23.0\pm3.5$	$13.7\pm3.6$	$4.9 imes10^{-3}$	$19.8 \pm 1.0$	$17.1 \pm 1.5$
$4.2  imes 10^{-6}$	$19.3\pm1.9$	$15.8 \pm 1.4$	$6.8  imes 10^{-3}$	$18.6\pm0.3$	$16.9\pm1.1$
$5.2  imes 10^{-6}$	$19.9 \pm 2.0$	$14.6\pm0.6$	$9.6  imes 10^{-3}$	$20.4\pm0.3$	$20.5\pm1.2$
$7.6  imes 10^{-6}$	$21.3\pm2.0$	$21.6\pm2.3$	$1.8 imes10^{-2}$	$17.0\pm1.7$	$16.6\pm0.5$
$1.9 imes10^{-5}$	$20.4\pm0.3$	$20.5\pm1.2$	$4.2  imes 10^{-2}$	$21.6\pm1.5$	$22.3\pm2.0$
$2.7  imes 10^{-5}$	$16.9\pm0.6$	$15.2\pm1.1$	$5.6 imes10^{-2}$	$20.0\pm2.0$	$22.6 \pm 2.9$
$3.8  imes 10^{-5}$	$16.5\pm1.4$	$15.8 \pm 1.7$	$7.5 imes10^{-2}$	$22.1\pm4.3$	$25.9\pm5.1$
mean	$19\pm3$	$17\pm4$	mean	$21\pm2$	$20\pm3$

<sup>*a*</sup> All through the experiment, the total concentration of trichloroacetate was 0.10 mol dm<sup>-3</sup>. <sup>*b*</sup> The concentration of TCA was held at 1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup> <sup>c</sup> The concentration of TPP was held at 1.90 × 10<sup>-5</sup> mol dm<sup>-3</sup>, and that of hydrogen ion was calculated from  $pK_a$  of TCA, 0.66. <sup>*d*</sup> d<sub>d</sub> and  $k_i$  denote the rate constants for the decrease of TPP and the increase of the diprotonated TPP, respectively.

of diprotonated TPP, fairly consistent with each other. The consistency between the values of  $19 \pm 3$  and  $17 \pm 4$  s<sup>-1</sup> is also acceptable, considering the poor reproducibility in the kinetic measurements under the various TPP concentrations. The averaged value for all data listed in Table 1 was  $19 \pm 3$  s<sup>-1</sup>. These results suggest the rate-determining step of the formation of the diprotonated TPP in the two-phase system to be the molecular diffusion process rather than the chemical reaction process. The reaction rate constants between porphyrins and hydrogen ion were reported to be larger than  $10^6$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> in homogeneous systems.<sup>9,12</sup>

In this dispersed two-phase system, we have to consider two types of diffusion process. The diffusion of hydrogen ions in the aqueous droplet phase to the dodecane-water interface is governed by spontaneous diffusion. On the other hand, the transport of TPP molecules in the dodecane phase is attained by a turbulent flow since the continuous dodecane phase is vigorously stirred by the mixing energy. However, even when the mixture was efficiently stirred, a stagnant layer of finite thickness located on the dodecane side of the interface can be assumed. Therefore, the one-dimensional random walk model was applied to the diffusion of hydrogen ion in the aqueous phase and the two-film theory to the diffusion of TPP in the stagnant layer, respectively, in order to estimate the time necessary for their diffusion to the interface.

According to the one-dimensional random walk model, the diffusion of hydrogen ions from the aqueous phase to the interface is represented by  $^{13}$ 

$$\bar{\Delta} = \sqrt{2D_{a}t} \tag{5}$$

where  $\Delta$ ,  $D_a$ , and *t* are the diffusion distance, the diffusion coefficient in an aqueous phase, and diffusion time, respectively.

<sup>(12)</sup> Pasternack, F. R.; Sutin, N.; Turner, H. D. J. Am. Chem. Soc. 1976, 98, 1908–1913.

<sup>(13)</sup> Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons, Inc.: New York, 1980; Chapter 5.

The devoted time in the transport process can be estimated by using eq 5 and a few assumptions. If we denote the saturated interfacial concentration of the diprotonated TPP on the interface of an aqueous droplet as *a*, multiplication of 2*a* by the surface area of a droplet gives the amount of hydrogen ion required for the protonation of all TPP molecules adsorbed at the interface. The relationship between the hydrogen ion concentration in the aqueous phase,  $c_{H^+}$ , and the amount of the hydrogen ion supplied to the interface for the protonation of TPP can then be described as follows:

$$c_{\rm H^+} \int_r^{t_0} 4\pi r^2 \, \mathrm{d}r = 2a4\pi {r_0}^2 \tag{6}$$

where  $r_0$  and r are the radius of a droplet and the distance from a center, respectively. The maximum diffusion distance of the hydrogen ion required for the interfacial protonation can be calculated from eq 6. A typical value of *a* for interfacially adsorbed species is  $10^{-8}$  mol dm<sup>-2</sup>.<sup>14</sup> The minimum value of  $c_{H^+}$  and radius of the aqueous droplet in this work are  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> and  $3.3 \times 10^{-3}$  cm, respectively. Thus  $\overline{\Delta}$  (i.e.,  $r_0 - r$ ) can be calculated as  $2 \times 10^{-4}$  cm. If we assume that  $D_a$  is the same value as the diffusion coefficient of acetic acid in 0.1 mol dm<sup>-3</sup> aqueous solution at 298 K,  $1.20 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>,<sup>15</sup> the devoted time in the transport process is obtained as ~2 ms. This value is vanishingly shorter than the time for achieving the protonation equilibrium. As a result of these estimation, we do not have to consider the diffusion of hydrogen ions from the bulk aqueous phase to the interface as the rate-determining step.

In liquid–liquid systems, the two-film theory of Lewis and Whitman has proved to be useful for dealing with a diffusion process.<sup>16</sup> This theory predicts that two stagnant layers exist in stirred liquid–liquid systems, one on either side of the interface with a thickness of  $\delta$ . In the present system, however, the stagnant layer model is not applied to the aqueous phase side, since the interior of the aqueous droplet phase is not stirred. In the stagnant layer on the organic phase, mass transfer occurs with only molecular diffusion of species, and Fick's first law for diffusion can be applied for the rate analysis. The rate equation for the diffusion of TPP to the interface is then written as

$$-\frac{\mathrm{d}[\mathrm{TPP}]_{\mathrm{o}}}{\mathrm{d}t} = \frac{D_{\mathrm{o}}S_{\mathrm{i}}}{\delta V_{\mathrm{o}}}[\mathrm{TPP}]_{\mathrm{o}}$$
(7)

where  $D_0$  is the diffusion coefficient of TPP in a dodecane phase. Equation 7 has the same form as the pseudo-first-order rate equation, eq 4, in which the term  $(D_0S_i/\delta V_0)$  is equated with the rate constant *k*. The thickness of the stagnant layer can be evaluated from the values of *k*,  $D_0$ , and  $S_i/V_0$ . The specific interfacial area,  $S_i/V_0$ , can be calculated by using the droplet radii of the dispersed phase, in which the volume of the dodecane phase

- (15) Landolt-Börnstein II Band, 5 Teil; Springer-Verlag: Berlin, 1968; pp 639– 653.
- (16) Danesi, P. R. In *Principles and Practices of Extraction*; Rydberg, J., Musikas, C., Choppin, R. G., Eds.; Marcel Dekker, Inc.: New York, 1992; Chapter 5.
- (17) Takami, K.; Saiki, H.; Tominaga, T.; Hirayama, S.; Scully, A. Proceedings of the 18th Symposium on Solution Chemistry of Japan; Kusatsu, Nov 3–5, 1995, pp 126–127.
- (18) Skelland, A. H. P. In Science and Practice of Liquid–Liquid Extraction, Vol. 1; Thornton, D. J., Ed.; Oxford University Press: New York, 1992; Chapter 2.



**Figure 4.** Schematic representation of the protonation of TPP at the dodecane—water interface. TPP molecule in the stagnant layer is provided from the continuous dodecane phase by the turbulent flow. The transport of TPP to the dodecane—water interface is dominated by only the molecular diffusion. The protonation of TPP proceeds at the interface, and the diprotonated TPP is adsorbed as the ion-pair with two trichloroacetate ions.

is the same as that of the aqueous phase. Provided that the distribution in droplet size is uniform over the whole system in the optical cell, the value of  $S_i/V_o$  was calculated as 777 cm<sup>-1</sup> by dividing the sum of interfacial area by the sum of each droplet volume.

The average droplet radius in the present system was  $(3.3 \pm 0.9) \times 10^{-3}$  cm. The diffusion coefficient of TPP in a dodecane phase is extrapolated from the values in several alkanes, measured by Tominaga et al.,<sup>17</sup> as  $3.5 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>. The rate constant of  $19 \text{ s}^{-1}$  yields  $1.4 \times 10^{-4}$  cm as the thickness of the stagnant layer. The values of the thickness previously reported range between  $1 \times 10^{-4}$  and  $1 \times 10^{-2}$  cm.<sup>18</sup> Because the present system is vigorously agitated for at least 1000 ms, the stagnant layer is thought to become very thin. The mechanism of the protonation of TPP at the dodecane–water interface is shown schematically in Figure 4.

In conclusion, the two-phase stopped-flow experiments on the diluted TPP in a dodecane—aqueous TCA system showed that the rate-determining step of the protonation of TPP is a molecular diffusion process of TPP within the stagnant layer in the dodecane phase with a rate constant of  $19 \text{ s}^{-1}$ . This value can be thought of as a limiting maximum value for the solvent extraction rate constant in a dodecane—water system. In other words, the interfacial reaction, with rate constant larger than  $19 \text{ s}^{-1}$ , must be leveled off in this system, and only a slower reaction can be assigned to the "true" interfacial chemical reaction. This conclusion has a practical importance in the assignment of the rate-determining step in the study of solvent extraction kinetics. Further studies to clarify the role of the liquid—liquid interfacial reaction in the solvent extraction mechanism are in progress.

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<sup>(14)</sup> Watarai, H.; Satoh, K. Langmuir 1994, 10, 3913-3915.

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