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Kinetics of the Racemization and Dissociation of Tris(1,10-phenanthroline)iron(II) and Tris(2,2′-bipyridine)iron(II) in Sodium Dodecyl Sulfate Solutions[1)]

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The kinetics of the racemization and dissociation of $[Fe(phen)_3]^{2+}$ (phen=1,10-phenanthroline) and $[Fe(bpy)_3]^{2+}$ (bpy=2,2′-bipyridine) was investigated in aqueous sodium dodecyl sulfate (SDS) solutions. The racemization and dissociation rates of the complexes increased with the increase in the SDS concentration to reach limiting values at concentrations above the critical micelle concentration (cmc). The rate changes occurring below the cmc were explained in terms of the formation of at least three kinds of premicellar aggregates of the complex ion with dodecyl sulfate ions. In the region slightly above the cmc, where the concentration of the complex ion is larger than that of the micelle, the rates continued to increase with the increase in the micellar concentration, suggesting that the complex ions interacted with the micelles. A comparison of the kinetic behavior in aqueous micellar solutions with that in organic solvents revealed that the complexes were located inside the micelle-water interface. The mechanisms of the acceleration in the micelle were discussed.

The micellar catalysis of chemical reactions has attracted much attention recently.[2)] Most of the studies reported so far have, however, been concerned with organic reactions. Relatively few are concerned with the reactions involving metal complexes.[2)] They include studies of the Hg^{2+}-induced aquation of $[CoCl(NH_3)_5]^{2+}$,[3)] the formation of Ni^{2+} and Mn^{2+} complexes with hydrophobic ligands,[4—6)] and electron-transfer reactions of hydrophobic metal complexes[7,8)] in sodium dodecyl sulfate (SDS) solutions. In all cases, changes in rate were observed in the regions of the SDS concentration both above and below the cmc. The changes in the rate above the cmc have been discussed as an example of micellar catalysis, but less attention has been paid to the changes in rate occurring below the cmc.

We previously studied the effects of alkyltrimethylammonium bromides[9)] and sodium 1-alkanesulfonates[10,11)] on the rates of the racemization and dissociation of $[Fe(phen)_3]^{2+}$ (phen=1,10-phenanthroline). Each of the cationic and the anionic surfactants affects the rates mainly at concentrations below the cmc. The rate changes were explained by the formation of premicellar aggregates of the complex ion with the surfactant ions. Above the cmc of each system, however, we could not specify whether or not the complex ion interacted with the micelles, since the rates remained almost unchanged above the cmc.

In this paper, we will report on kinetic studies of the racemization and dissociation of $[Fe(phen)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ (bpy=2,2′-bipyridine) in SDS solutions; investigations were made to elucidate the nature of the interaction of the complex ions with monomeric and micellar dodecyl sulfate ions below and above the cmc, and to clarify the dependence of the racemization and dissociation rates on the SDS concentration.

Experimental

The synthesis and optical resolution of $(+)_{589}$-$[Fe(phen)_3](ClO_4)_2\cdot 2H_2O$[12)] and $(+)_{589}$-$[Fe(bpy)_3](ClO_4)_2\cdot 2H_2O$[13)] were carried out according to the method of Dwyer and Gyarfas; $[\alpha]_{589}=1400°$ and $[\alpha]_{589}=4900°$. Sodium dodecyl sulfate from Merck (for tenside test) was recrystallized five times from ethanol and then dried under reduced pressure. Sodium chloride from Merck (Suprapur) and hydrochloric acid from Wako (Super Special Grade) were used without further purification. The kinetic measurements were carried out at 25.0 °C with the perchlorate of each complex ([complex]= 5×10^{-5} mol dm^{-3}) in solutions containing SDS[14)] with and without NaCl ([NaCl]=0, 0.02, 0.15, 0.40, and 1.00 mol dm^{-3}). The dissociation rates of the complexes were observed in the presence of 5.0×10^{-4} mol dm^{-3} nickel(II) chloride, except for the systems containing HCl. (Both Ni^{2+} and H^+ are effective scavengers for the ligands released during the reactions.) The racemization rates of $[Fe(phen)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ were observed by following the optical rotation of the solutions at 546 and 589 nm, and their dissociation rates, by following the absorbance at 510 and 520 nm, respectively. Multiple measurements under the same experimental conditions gave rate constants reproducible within ±5% and ±1% respectively for the racemization and dissociation of the complexes. The other reagents and procedures were described in our previous paper.[15)]

Results and Discussion

Interaction of $[Fe(phen)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ with Dodecyl Sulfate Ions Below cmc. *Rate Behavior of the Complexes in SDS Solutions*: Figure 1 shows the observed racemization and dissociation rate constants of $[Fe(phen)_3]^{2+}$ against the SDS concentration in the absence and the presence of NaCl (0, 0.02 and 0.15 mol dm^{-3}). The dissciation rate of the complex slightly decreased, and the racemization rate slightly increased, with the increase at SDS concentrations below 0.3×10^{-3} mol dm^{-3}. In the range of (0.3—1.0) $\times10^{-3}$ mol dm^{-3}, the rates increased steeply with the increase in the SDS concentration in the presence of NaCl, while the dodecyl sulfate of the complex was precipitated in this range of SDS concentrations in the absence of NaCl. Such a precipitation has also been reported for the $[Ru(bpy)_3]^{2+}$-SDS system[16)]. At SDS concentrations higher than 1×10^{-3} mol dm^{-3}, the increases in the rates became less steep and reached the limiting values within the range of experimental uncertainty at the SDS concentration characteristic of

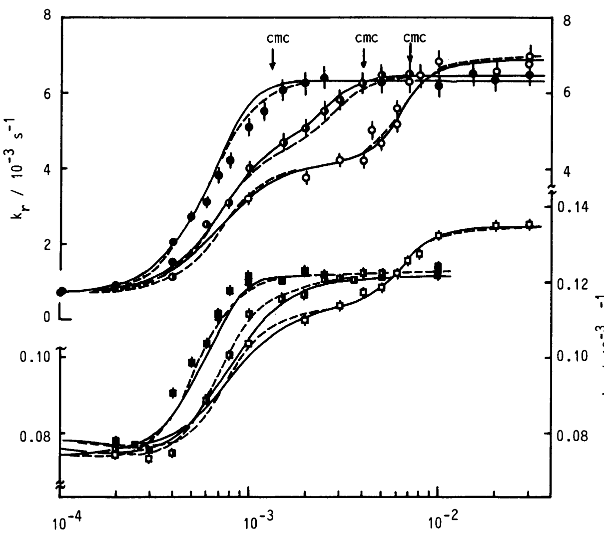

Fig. 1. Plots of the rate constants for the racemization (circles) and dissociation (squares) of $[Fe(phen)_3]^{2+}$ against the logarithm of SDS concentration. ○, □: No NaCl; ○, □: $[NaCl]=0.02\,mol\,dm^{-3}$; ●, ■: $[NaCl]=0.15\,mol\,dm^{-3}$. The solid ($m=3$) and broken ($m=4$) curves are those calculated by substituting the parameter values (Table 1) into Eq. 1.

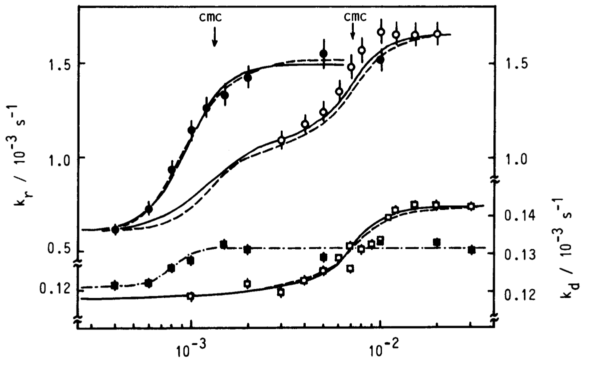

Fig. 2. Plots of the rate constants for the racemization (circle) and dissociation (square) of $[Fe(bpy)_3]^{2+}$ against the logarithm of SDS concentration. ○, □: No NaCl; ●, ■: $[NaCl]=0.15\,mol\,dm^{-3}$. The solid ($m=3$) and broken ($m=4$) curves are those calculated by substituting the parameter values (Table 1) into Eq. 1.

the system. Similar features are shown by $[Fe(bpy)_3]^{2+}$, as is depicted in Fig. 2. With the rate changes of the complexes in SDS solutions, the absorption spectra of the complexes changed slightly in a fashion similar to that reported for the $[Fe(phen)_2(CN)_2]$-SDS system.[7)]

Formation of the Premicellar Aggregates of the Complex Ions with Dodecyl Sulfate Ions: The cmc values of the SDS solutions containing the complex ions[17)] are indicated by arrows in Figs. 1 and 2. Since the rate change in each system occurred mainly below the respective cmc, the change may be accounted for by the formation of the premicellar aggregates of the complex ions with dodecyl sulfate ions, and not by the interaction of the complex ions with micelles. The same applies to the spectral changes accompanied by the rate changes. This is in contrast to the previous reports on the $[Fe(phen)_2(CN)_2]$, $[Fe(phen)_2(CN)_2]^+$, and $[Ru(bpy)_3]^{2+}$[16)] systems, in which the spectral changes of the complexes in SDS solutions were related to the incorporation of the complexes into SDS micelles.[7,8,16)]

Analysis of the Kinetic Results: The racemization and dissociation rates of $[Fe(phen)_3]^{2+}$ changed with the SDS concentration in at least three steps (Fig. 1): changes in the regions of the SDS concentrations below $0.3\times10^{-3}\,mol\,dm^{-3}$, changes between 0.3 and $1.0\times10^{-3}\,mol\,dm^{-3}$ and changes higher than $1\times10^{-3}\,mol\,dm^{-3}$. The rate changes of the three steps can be related to the formation of at least three kinds of aggregates of the complex ion with dodecyl sulfate ions.

By analogy with the previous results for the $[Fe(phen)_3]^{2+}$-1-dodecanesulfonate[11)] and $[Ni(phen)_3]^{2+}$-1-dodecanesulfonate systems,[18)] the first step in the rate change can be attributed to the formation of the 1:1 aggregate of the complex ion and the dodecyl sulfate ion, and the second and third steps, to the formation of 1:3 or 1:4 and 1:8 aggregates. Then, the gross rate constant, k, can be expressed as:

$$k = \frac{k_0 + k_1\beta'_1[DS^-] + k_m\beta'_m[DS^-]^m + k_8\beta'_8[DS^-]^8}{1 + \beta'_1[DS^-] + \beta'_m[DS^-]^m + \beta'_8[DS^-]^8}, \tag{1}$$

where k_0, k_1, k_m, and k_8 represent the rate constants of the complex ion aggregated with zero, one, m ($m=3$ or 4), and eight dodecyl sulfate ions respectively. The β'_1, β'_m, and β'_8 mean the gross concentration formation constants for the aggregates of the complex ion with one, m, and eight dodecyl sulfate ions respectively, and $[DS^-]$, the concentration of free dodecyl sulfate ions.

In the analysis of the kinetic data for the $[Fe(phen)_3]^{2+}$- SDS system, the values of β'_1, k_{1r} (k_1 for racemization), and k_{1d} (k_1 for dissociation) were assumed to be equal to the corresponding values for the $[Fe(phen)_3]^{2+}$-1-dodecanesulfonate system, *i.e.*, $k_{1r}=2.1\times10^{-3}\,s^{-1}$, $k_{1d}=0.026\times10^{-3}\,s^{-1}$, and $\beta'_1=270$, 220, and $170\,mol^{-1}\,dm^3$ for systems without NaCl, with $[NaCl]=0.02$, and $0.15\,mol\,dm^{-3}$ respectively.[11)] With these parameter values, the kinetic results at low SDS concentrations were analyzed graphically by disregarding the formation of the 1:8 aggregate. The transformation of Eq. 1 disregarding the $[DS^-]^8$ terms leads to this relation:

$$k = k_m - \frac{1}{\beta'_m}\frac{(k-k_0) + (k-k_1)\beta'_1[DS^-]}{[DS^-]^m}. \tag{2}$$

Plots of k *vs.* $\{(k-k_0)+(k-k_1)\beta'_1[DS^-]\}/[DS^-]^m$ should give a straight line with a slope of $-1/\beta'_m$ and an intercept of k_m for $m=3$ and 4. The transformation of Eq. 1 (including the $[DS^-]^8$ terms) leads to this relation:

$$k = k_8 - \frac{1}{\beta'_8}\frac{(k-k_0) + (k-k_1)\beta'_1[DS^-] + (k-k_m)\beta'_m[DS^-]^m}{[DS^-]^8} \tag{3}$$

The k_8 and β'_8 values were obtained by plotting the rate constants at high SDS concentrations against the ratio appearing at the extreme right of Eq. 3. Then, the sets of the k_m, β'_m, k_8, and β'_8 values for $m=3$ and 4 were recalculated by the least-squares fit[19)] of Eq. 1 to the kinetic data; they are given in Table 1. These values were

TABLE 1. FORMATION CONSTANTS OF THE 1 : m (m=3 OR 4) AND 1 : 8 AGGREGATES OF $[Fe(phen)_3]^{2+}$ OR $[Fe(bpy)_3]^{2+}$ AND DODECYL SULFATE IONS, AND THE RACEMIZATION AND DISSOCIATION RATE CONSTANTS OF THE COMPLEXES IN THE AGGREGATES IN MEDIA WITH DIFFERENT NaCl CONCENTRATIONS$^{a)}$

Complex	[NaCl] / mol dm^{-3}	m	log $\beta_m'^{b)}$	log $\beta_8'^{b)}$	$10^3k_{mr}/s^{-1}$	$10^3k_{md}/s^{-1}$	$10^3k_{8r}/s^{-1}$	$10^3k_{8d}/s^{-1}$
$[Fe(phen)_3]^{2+}$	0	3	9.5±0.1	20.4±0.2	4.2±0.1	0.115±0.001	6.8±0.2	0.135±0.001
		4	12.5±0.1	21.4±0.2	4.0±0.1	0.113±0.001	6.9±0.2	0.135±0.001
	0.02	3	9.5±0.1	22.3±0.4	5.1±0.2	0.121±0.002	6.4±0.2	0.122±0.001
		4	12.7±0.1	22.9±0.4	4.4±0.3	0.119±0.002	6.5±0.3	0.123±0.003
	0.15	3	9.8±0.1	25.2±0.2	5.1±0.3	0.120±0.002	6.3±0.1	0.122±0.001
		4	13.3±0.1	25.4±0.3	4.3±0.3	0.114±0.006	6.4±0.1	0.122±0.001
$[Fe(bpy)_3]^{2+}$	0	3	8.7±0.3	19.5±0.4	1.13±0.04	0.121±0.001	1.65$^{c)}$	0.142$^{c)}$
		4	11.6±0.4	20.2±0.4	1.07±0.04	0.121±0.001	1.65$^{c)}$	0.142$^{c)}$
	0.15	3	9.2±0.1	24.0±0.1	1.19±0.09	—	1.48±0.02	—
		4	12.4±0.1	23.9±0.2	1.21±0.08	—	1.51±0.03	—

a) The parameter values of k_{0r}=0.65, k_{0d}=0.0794, 0.0757, and 0.0746, of k_{1r}=2.1, k_{1d}=0.026/10^{-3} s^{-1}and of β_1'=270, 220, and 170 for systems of [NaCl]=0, 0.02, and 0.15 mol dm^{-3} respectively, were assumed for the analysis of the results for $[Fe(phen)_3]^{2+}$-SDS systems. The values of k_{0r}=0.61 and 0.59, and of k_{0d}=0.118 and 0.122/10^{-3} s^{-1} for systems of [NaCl]=0 and 0.15 mol dm^{-3} respectively, and β_1'=0 were assumed for $[Fe(bpy)_3]^{2+}$-SDS systems. b) Average values obeained from racemization and dissociation experiments. c) Average values of the rate constants in solutions of the SDS concenration higher than 0.012 mol dm^{-3}. These values were assumed for the analysis.

used to calculate the k_r and k_d values, which are shown as the solid (for m=3) and broken (for m=4) curves in Fig. 1.

The changes in the racemization and dissociation rates of $[Fe(bpy)_3]^{2+}$ (Fig. 2) with the SDS concentration are similar to those for $[Fe(phen)_3]^{2+}$(Fig. 1). This suggests that the mechanisms of the rate changes are similar between the two complexes. Since the k_1 and β_1' values for the $[Fe(bpy)_3]^{2+}$-SDS or similar systems were not available, and since the formation of the 1:1 aggregate showed only a small effect on the measured reaction rates (as may be seen from the rate changes at low concentrations in Fig. 2), the kinetic results for the system were analyzed by disregarding the formation of the 1:1 aggregate. The disregard of the formation of the 1:1 aggregate for the $[Fe(phen)_3]^{2+}$-SDS system has little effect on the k_m, k_8, β_m', and β_8' values, although it enlarged the difference between the observed and the calculated rate constants at low SDS concentrations. For the $[Fe(bpy)_3]^{2+}$-SDS system, the calculated rate constants based on the parameter values obtained by disregarding the formation of the 1:1 aggregate agreed well with the observed values at low SDS concentrations (Fig. 2), showing that the approximation for the analysis was reasonably good. The results of the analysis for this system are listed in Table 1.

Table 1 shows that the aggregate formation constants, β_m' and β_8', are larger for systems with added NaCl than those without NaCl and larger for systems containing $[Fe(phen)_3]^{2+}$ than those containing $[Fe(bpy)_3]^{2+}$. This is natural since hydrophobic interaction is more pronounced in NaCl solutions than in solutions without NaCl, and phen is more hydrophobic than bpy.

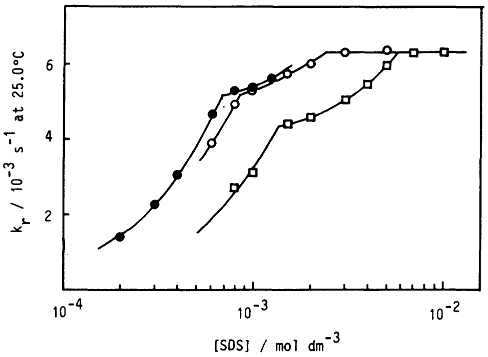

Fig. 3. Plot of the racemization rate constants of $[Fe(phen)_3]^{2+}$ against the logarithm of SDS concentration. ○, [NaCl]=0.4 mol dm^{-3}, $[Fe(phen)_3^{2+}]$=5×10^{-5} mol dm^{-3}; ●, [NaCl]=1.0 mol dm^{-3}, $[Fe(phen)_3^{2+}]$=5×10^{-5} mol dm^{-3}; □, [NaCl]=0.15 mol dm^{-3}, $[Fe(phen)_3^{2+}]$ =2.5×10^{-4}mol dm^{-3}.

Interaction of $[Fe(phen)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ with SDS Micelles Above cmc. The phenomenon that the rates changed below the cmc, while they remained almost constant above the cmc, suggests that the complex ions did not interact with micelles or that the reactivities of the complexes in the micelles were nearly the same as those in the aggregates. In order to clarify whether or not the complex ions interacted with the micelles, we measured the racemization rates of $[Fe(phen)_3]^{2+}$ in NaCl solutions ([NaCl]=0.4 and 1.0 mol dm^{-3} with [complex]=5×10^{-5} mol dm^{-3} and [NaCl]=0.15 mol dm^{-3} with [complex]=25×10^{-5} mol dm^{-3}, Fig. 3). In each case, the rate increased with an increase in the SDS concentration, steeply in the first region and then linearly and less steeply in the second region, until the rate reached a limiting value. Two break points were clearly observed. The SDS concentration at the first break point roughly corresponds to the cmc value,[20,21] suggesting that the micelles participated in the rate increase at the second step. The linear rate increase in the second region and the sharpness of the second break indicate that the association constant of the complex ions with the micelles is large and that the

TABLE 2. THE RATE CONSTANTS ($k/10^{-3}\ s^{-1}$) AND THE ACTIVATION PARAMETERS OF RACEMIZATION OF $[Fe(phen)_3]^{2+}$ AND $[Fe(bpy)_3]^{2+}$ IN AQUEOUS AND MICELLAR SOLUTIONS

T/°C	$[Fe(phen)_3]^{2+}$		$[Fe(bpy)_3]^{2+}$	
	Without SDS	With SDS a)	Without SDS	With SDS a)
12.0	—	1.09(5) b)	—	—
15.0	—	1.73(8)	—	—
17.5	—	2.4(1)	—	—
20.0	0.30(1)	3.6(1)	0.26(1)	0.72(3)
22.5	0.42(2)	4.7(2)	0.39(2)	1.08(5)
25.0	0.65(3)	6.6(3)	0.61(3)	1.65(8)
27.5	1.00(5)	10.2(5)	0.92(4)	2.3(1)
30.0	1.53(7)	—	1.36(6)	3.3(1)
32.5	2.3(1)	—	1.98(9)	4.9(2)
35.0	3.4(1)	—	2.9(1)	6.9(3)
$\Delta H^{\neq}$ / kJ mol^{-1}	122.5(0.6) b)	98.6(1.4)	119.4(0.6)	109.9(0.7)
$\Delta S^{\neq}$ / J K^{-1} mol^{-1}	105(2)	43(6)	94(2)	70(2)

a) 0.02 mol dm^{-3}. b) The values in parentheses are the standard deviations.

association with the micelles was completed at the second break point. The number of $[Fe(phen)_3]^{2+}$ per micelle was calculated on the basis of the micellar concentration at the second break point and the concentration of the complex to be 6.7 and 4.3 in 0.15 and 0.4 mol dm^{-3} NaCl solutions respectively.22) A similar number, 4.1, was reported for the $[Ru(bpy)_3]^{2+}$–SDS system.16)

Location of the Complex Ions in a Micelle: The limiting rate of the racemization and dissociation of $[Fe(phen)_3]^{2+}$ in SDS solutions were, respectively, 10 and 1.7 times the rates in pure water, while those of $[Fe(bpy)_3]^{2+}$ were, respectively, 2.8 and 1.2 times the rates in pure water (Figs. 1 and 2). Similar increases in the reaction rates were also observed when the complex ions were dissolved in organic solvents23–25) or were in contact with alkyl groups.9,11) By analogy, the complex ions in the micelle are in contact with the alkyl chains of the dodecyl sulfate ions. Table 2 lists the rate constants at various temperatures for the racemization of the complexes in micellar solutions and in pure water, as well as the activation parameters. Figure 4 shows a plot of the activation enthalpy *vs.* the activation entropy for the racemization of $[Fe(phen)_3]^{2+}$ in aqueous and in alcohol-water solutions.26) The fact that the activation parameters for the racemization of $[Fe(phen)_3]^{2+}$ in the micellar solution are close to those in pure butanols and in concentrated aqueous ethanol (0.90 mol. fraction) suggests that the complex ions were located inside the micelle–water interface or at the "Stern region"27,28) of the micelle, and not on the interface. The activation parameters for $[Fe(bpy)_3]^{2+}$ also showed a similar, though less pronounced, tendency.

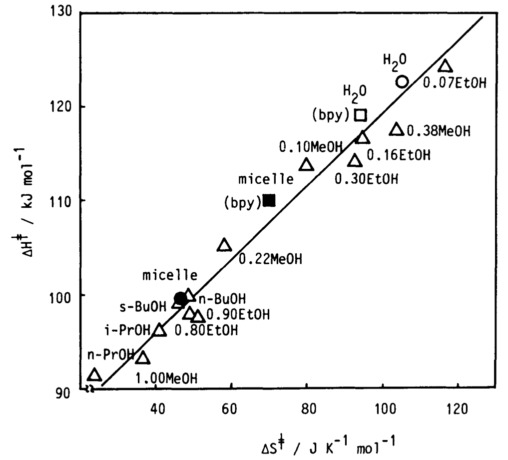

Fig. 4. Plot of activation enthalpy *vs.* activation entropy for the racemization of $[Fe(phen)_3]^{2+}$ (circle) and $[Fe(bpy)_3]^{2+}$ (square) in aqueous and micellar solutions and for the racemization of $[Fe(phen)_3]^{2+}$ in alcohol-water and alcohol solutions. ○, □: No SDS, no NaCl; ●, ■: 2×10^{-2} mol dm^{-3} SDS, no NaCl; △: alcohol-water (mole fraction of the alcohol is shown) and alcohol solutions.

Mechanism of Acceleration of the Reactions in the Micelle: The racemization of the complexes is known to proceed by means of an intramolecular twist mechanism in organic solvents.25) The same is probably true for the complexes in the micelle. Table 2 shows that the higher rate of the racemization in micelles was brought about by the decrease in the activation enthalpy, though this decrease was partially compensated for by the decrease in the activation entropy. This can be related to the hydrophobic nature of the complex ions. In an aqueous solution, a cage-like "iceberg" structure formed around the complex ions9) has to be broken for the complex ions to racemize, while no such iceberg structure is formed in the micelles and both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are expected to be smaller.

The dissociation rates of the complexes increased in the micelle, though the increase was much less pronounced than that of the racemization rates. The higher rate of the dissociation of $[Fe(phen)_3]^{2+}$ in the micelle is related mainly to a smaller activation enthalpy, and that of $[Fe(bpy)_3]^{2+}$, to a larger activation entropy (Table 3). This difference may be due to the difference in the mechanism of the dissociation between the two complexes; in the latter complex, dissociation

TABLE 3. THE RATE CONSTANTS ($k/10^{-3}$ s^{-1}) AND THE ACTIVATION PARAMETERS OF DISSOCIATION OF $[Fe(phen)_3]^{2+}$ AND $[Fe(bpy)_3]^{2+}$ IN AQUEOUS AND MICELLAR SOLUTIONS

T/°C	$[Fe(phen)_3]^{2+}$		$[Fe(bpy)_3]^{2+}$	
	Without SDS	With SDS[a]	Without SDS	With SDS[a]
15.0	0.0188(1)[b]	0.0227(2)	0.0212(2)	0.0249(2)
20.0	0.0307(3)	0.0566(6)	0.0501(5)	0.0601(6)
25.0	0.0794(8)	0.135(1)	0.118(1)	0.143(1)
30.0	0.178(2)	0.316(3)	0.266(3)	0.329(3)
$\Delta H^{\ast}$ / kJ mol^{-1}	128.4(0.9)[b]	124.6(1.3)	119.5(1.4)	122.0(1.1)
$\Delta S^{\ast}$ / J K^{-1} mol^{-1}	107(3)	99(5)	81(6)	91(4)

a) [SDS]=0.020 mol dm^{-3}. b) The values in parentheses are the standard deviations.

probably occurs through a five-coordinate intermediate with an open bipyridine chelate ring.

Kinetics and Mechanism of Dissociation of $[Fe(bpy)_3]^{2+}$ in Acidic Micellar Solutions: The increase in the HCl concentration increased the dissociation rate of $[Fe(bpy)_3]^{2+}$ in solutions with (1×10^{-2} mol dm^{-3}) and without SDS (Fig. 5). The rate changes with the HCl concentration can be described by the mechanism proposed by Basolo *et al.* (Fig. 6).[29] According to this mechanism, the dissociation rate constant, k', is expressed by:

$$k' = \frac{k'_1(k'_2 + k'_3[\mathrm{H^+}])}{k'_{-1} + k'_2 + k'_3[\mathrm{H^+}]}, \tag{4}$$

where k'_1, k'_{-1}, k'_2, and k'_3 are the rate constants for the reaction steps shown in Fig. 6. When $[\mathrm{H^+}]$ is sufficiently low, the value of k' will be approximately equal to the limiting value given by:

$$k'_0 = k'_1\left(\frac{k'_2}{k'_{-1} + k'_2}\right). \tag{5}$$

Then Eq. 4 is transformed to:

$$k' = k'_1 - \frac{k'_{-1} + k'_2}{k'_3}\,\frac{k' - k'_0}{[\mathrm{H^+}]}. \tag{6}$$

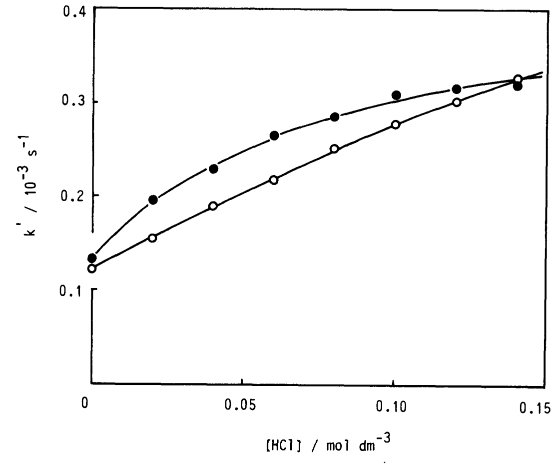

Fig. 5. Acid dependences of the dissociation rate constant of $[Fe(bpy)_3]^{2+}$ in aqueous and micellar solutions (I=0.15, NaCl): ○, No SDS; ●, 1×10^{-2} mol dm^{-3} SDS.

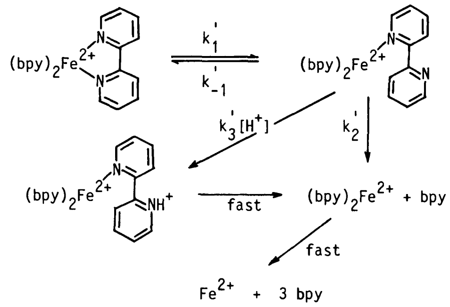

Fig. 6. Reaction scheme of the acid dependent dissociation of $[Fe(bpy)_3]^{2+}$.

TABLE 4. RESULTS OF THE ANALYSIS OF THE ACID DEPENDENCE OF THE DISSOCIATION RATE OF $[Fe(phen)_3]^{2+}$ IN AQUEOUS AND MICELLAR SOLUTIONS

	[SDS]=0	[SDS]=0.01 mol dm^{-3}
k_1' / 10^{-3} s^{-1}	1.3±0.5	0.44±0.03
k_2'/k'_{-1}	0.10±0.05	0.43±0.04
k_3'/k'_{-1} / mol^{-1} dm^3	1.8±1.1	18.1±4.3

The k' values were plotted against $(k' - k'_0)/[\mathrm{H^+}]$ to give a straight line with a slope of $-(k'_{-1}+k'_2)/k'_3$ and an intercept of k'_1. These values, together with the k'_0 ($=k'_1k'_2/(k'_{-1}+k'_2)$) value, gave the k'_2/k'_{-1} and k'_3/k'_{-1} values listed in Table 4. The table shows that the rate constant of the formation of a five-coordinate intermediate with an open bipyridine chelate ring, k'_1, is smaller in the presence of SDS than in its absence. In spite of this lower rate of intermediate formation, the dissociation rate of the complex was higher in the solution containing SDS (Fig. 5, for $[\mathrm{H^+}]\leqq0.14$ mol dm^{-3}) because of the larger fraction of the intermediate undergoing dissociation (because of the larger $(k'_2+k'_3[\mathrm{H^+}])/(k'_{-1}+k'_2+k'_3[\mathrm{H^+}])$ value).

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