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Kinetics of the Racemization of Tris(1,10-phenanthroline)nickel(II). Hydrophobic Interaction of the Complex Ion with 1-Alkanesulfonate Ions

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The kinetics of the racemization of $[Ni(phen)_3]^{2+}$ were investigated in the presence of 1-alkanesulfonate ions (n-$C_nH_{2n+1}SO_3^-$; $n=8$, 10, 12, and 14). The racemization rate decreased with the increase in the alkanesulfonate concentrations in the region of low sulfonate concentrations; then, in the region of higher concentrations, it began to increase, but it never exceeded the rate in water. The rate changes at low and high alkanesulfonate concentrations were related to the formation of the 1 : 1 and 1 : m aggregates of the complex ion with alkanesulfonate ions respectively. A comparison of the aggregate formation constants of $[Ni(phen)_3]^{2+}$ with those of $[Fe(phen)_3]^{2+}$ confirmed that hydrophobic interaction is responsible for the aggregate formation. The energy of hydrophobic interaction between $[Ni(phen)_3]^{2+}$ and an alkanesulfonate ion was estimated to be 1.0 ± 0.1 kJ mol^{-1} per methylene group of the latter. The kinetic behavior of the racemization of $[Ni(phen)_3]^{2+}$ in the aggregates was also compared with those of the racemization and dissociation of $[Fe(phen)_3]^{2+}$, and it was discussed in relation to the racemization mechanism of $[Ni(phen)_3]^{2+}$. The reaction rates of the complexes in D_2O solutions were also reported.

Aromatic diimines, such as 1,10-phenanthroline and 2,2′-bipyridine, are among the most important ligands in coordination chemistry. Because of their hydrophobicity, metal complexes of these ligands show unique interactions with hydrophobic solutes in aqueous solutions.[1–3]

We previously measured the effects of alkylammonium cations[4] and 1-alkanesulfonate anions[5,6] on the rates of racemization and dissociation of $[Fe(phen)_3]^{2+}$. The results at low organic-ion concentrations were related satisfactorily to the formation of the 1 : 1 aggregates of the complex and organic ions caused by hydrophobic interactions. In solutions of higher alkanesulfonate concentrations, the rate behavior of the complex was related to the formation of the 1 : m aggregates of the complex and alkanesulfonate ions.

One object of the present work is to confirm the formation of the aggregates of the tris(1,10-phenanthroline)metal ion with alkansulfonate ions and to see whether the aggregate formation occurs entirely by means of electrostatic and hydrophobic interactions or by any other interactions specific for the metal ion of the chelate. Another object is to disclose the effect of RSO_3^- on the racemization rate of $[Ni(phen)_3]^{2+}$. A comparison of the effect with those of RSO_3^- on the racemization and dissociation rates of $[Fe(phen)_3]^{2+}$ previously obtained[6] will give information regarding the racemization mechanism of $[Ni(phen)_3]^{2+}$.[7]

Experimental

The synthesis and optical resolution of $(-)_{589}$-$[Ni(phen)_3](ClO_4)_2\cdot3H_2O$ was carried out according to the method of Dwyer and Gyarfas;[8] $[\alpha]_{589}=-1400°$. Deutrium oxide was supplied by the Aldrich Chemical Co. (99.8 atom% D). Racemization rates were obtained at 25.0 °C by following the decrease in the optical rotation (405 nm) of the solution, containing 5×10^{-5} mol dm^{-3} of the optically active complex as perchlorate and a proper concentration of 1-alkanesulfonate, on a Union PM101 automatic polarimeter. The reactions were followed for two to four half-lives. They were first order in the concentration of the metal complex in the time range studied. The racemization-rate constant was defined as $k_r=[\ln(\alpha_0/\alpha_t)]/t$, where α_0 and α_t represent the optical rotations at times zero and t respectively, and was calculated by the usual method for the first-order reactions. The racemization and dissociation rates of $[Fe(phen)_3]^{2+}$ in H_2O and D_2O were obtained at 25.0 °C with 5×10^{-5} mol dm^{-3} $[Fe(phen)_3](ClO_4)_2$ in a way similar to that described in our previous paper.[6] The other chemicals and procedures were the same as those described previously.[6]

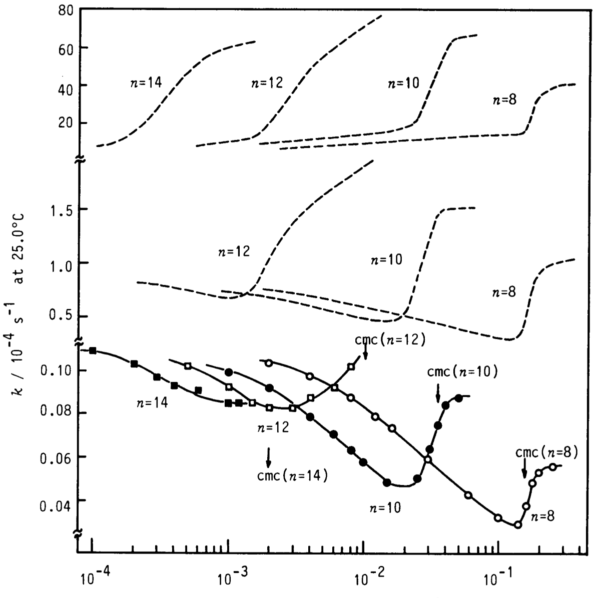

Fig. 1. The racemization rate constants of $[Ni(phen)_3]^{2+}$ (5×10^{-5} mol dm^{-3}) in the presence of sodium alkanesulfonates: ○, n-$C_8H_{17}SO_3Na$; ●, n-$C_{10}H_{21}SO_3Na$; □, n-$C_{12}H_{25}SO_3Na$; ■, n-$C_{14}H_{29}SO_3Na$. The solid curves show the values calculated on the basis of Eq. 8. The arrows indicate the cmc values for each sodium alkanesulfonate. The broken curves give the results previously obtained for the dissociation (middle) and racemization (top) of $[Fe(phen)_3]^{2+}$.

TABLE 1. THE AGGREGATION NUMBER OF ALKANESULFONATE (m) IN THE AGGREGATE WITH $[Ni(phen)_3]^{2+}$ AND THE AGGREGATE FORMATION CONSTANTS OF THE 1 : 1 (K_1) AND 1 : m (β'_m) AGGREGATE OF THE COMPLEX WITH ALKANESULFONATE AT 25.0 °C[a)]

Alkanesulfonate	K_1/mol^{-1} dm^3	m	log(β'_m/mol^{-m} dm^{3m})
n-$C_8H_{17}SO_3^-$	54±4 (70±14)	14±2 (14±2)	11.7±1.6 (11.8±1.6)
n-$C_{10}H_{21}SO_3^-$	164±14 (177±34)	8±1 (8±1)	12.8±1.6 (13.1±1.2)
n-$C_{12}H_{25}SO_3^-$[b)]	280±80 (320±40)	3 (3—4)	8.7±0.4[c)] (8.0—10.8)
		8 (8)	19.5±0.5[c)] (18.0—19.0)
n-$C_{14}H_{29}SO^{3-}$	430±390 (770±120)	3±1 (3—4)	10.5±3.5 (10.8—14.4)

a) The values in parentheses are those for the systems of $[Fe(phen)_3]^{2+}$–alkanesulfonates (from Ref. 6). b) The m values for this system are assumed to be equal to the values for the systems containing decane- and tetradecanesulfonate. c) These values were obtained by assuming k_3 and k_8 to be equal to 0.83 and 1.10 respectively.

Results

In Fig. 1, the measured rate constants of the racemization of $[Ni(phen)_3]^{2+}$ are plotted against the logarithm of the alkanesulfonate-ion concentration. The racemization and dissociation rate constants of $[Fe(phen)_3]^{2+}$ previously obtaind are also shown in the figure. A comparison of the profiles of the rate changes of the two complexes suggests that the rate behavior of $[Ni(phen)_3]^{2+}$ may be explained in a fashion similar to the case of $[Fe(phen)_3]^{2+}$;[5,6] the complex ion forms the 1:1 and 1:m ($m \geqq 2$) aggregates with alkanesulfonate ions in the regions of low and high alkanesulfonate concentrations respectively. Then, the following mechanism can be considered:

$$(-)\text{-}[Ni(phen)_3]^{2+} + RSO_3^- \xrightleftharpoons{\beta'_1} (-)\text{-}[Ni(phen)_3]^{2+}\cdot RSO_3^-, \tag{1}$$

$$(-)\text{-}[Ni(phen)_3]^{2+} + m\,RSO_3^- \xrightleftharpoons{\beta'_m} (-)\text{-}[Ni(phen)_3]^{2+}\cdot m\,RSO_3^- \tag{2}$$

$$(-)\text{-}[Ni(phen)_3]^{2+} \xrightarrow{k_0} rac\text{-}[Ni(phen)_3]^{2+}, \tag{3}$$

$$(-)\text{-}[Ni(phen)_3]^{2+}\cdot RSO_3^- \xrightarrow{k_1} rac\text{-}[Ni(phen)_3]^{2+}\cdot RSO_3^-, \tag{4}$$

$$(-)\text{-}[Ni(phen)_3]^{2+}\cdot m\,RSO_3^- \xrightarrow{k_m} rac\text{-}[Ni(phen)_3]^{2+}\cdot m\,RSO_3^- \tag{5}$$

$$\beta'_1 = \frac{[Ni(phen)_3{}^{2+}\cdot RSO_3^-]}{[Ni(phen)_3{}^{2+}][RSO_3^-]} = K_1\frac{f_2 f_1}{f_1}, \tag{6}$$

$$\beta'_m = \frac{[Ni(phen)_3{}^{2+}\cdot m\,RSO_3^-]}{[Ni(phen)_3{}^{2+}][RSO_3^-]^m}, \tag{7}$$

where k_0, k_1, and k_m represent the rate constants of the complex cation associated with zero, one, and m alkanesulfonate ions respectively, and where f_z shows the activity coefficient of an ion as a function of its charge ($\pm z$).[9] Therefore, the racemization rate constant is expressed by:

$$k = \frac{k_0 + k_1\beta'_1[RSO_3^-] + \sum_{m=2}^{\infty} k_m\beta'_m[RSO_3^-]^m}{1 + \beta'_1[RSO_3^-] + \sum_{m=2}^{\infty}\beta'_m[RSO_3^-]^m}. \tag{8}$$

The kinetic results were analyzed on the basis of Eq. 8 in a way similar to that used for the $[Fe(phen)_3]^{2+}$–RSO_3^- system.[6] The k_0, k_1, K_1 ($=\beta'_1/f_2$), m, k_m, and β'_m values thus obtained are listed in Tables 1 and 2. They were substituted into Eq. 8 to calculate the solid curves in Fig. 1.

The rate constants of the racemization of $[Ni(phen)_3]^{2+}$, as well as those of the racemization and dissociation of $[Fe(phen)_3]^{2+}$, as measured in H_2O and D_2O solutions, are listed in Table 3.

TABLE 2. RACEMIZATION RATE CONSTANTS OF $[Ni(phen)_3]^{2+}$ IN THE 1 : 1 AND 1 :m AGGREGATES OF THE COMPLEX ION WITH ALKANESULFONATE IONS[a)]

Alkanesulfonate	k_1	k_m	m
None	(k_0=0.113±0.002)	—	—
n-$C_8H_{17}SO_3^-$	0.005±0.005	0.057	14
n-$C_{10}H_{21}SO_3^-$	0.010±0.005	0.089	8
n-$C_{12}H_{25}SO_3^-$	(≈0.010)	>0.110	8
		≈0.083	3
n-$C_{14}H_{29}SO_3^-$	(≈0.010)	0.842±0.002	3

a) $k/10^{-4}$ s^{-1} at 25.0 °C.

TABLE 3. THE REACTION RATE CONSTANTS OF $[Ni(phen)_3]^{2+}$ AND $[Fe(phen)_3]^{2+}$ IN H_2O AND D_2O SOLUTIONS AT 25.0°C

	$k/10^{-4}$ s^{-1} in H_2O	$k/10^{-4}$ s^{-1} in D_2O	$\frac{k\,(D_2O)}{k\,(H_2O)}$
$[Ni(phen)_3]^{2+}$			
racemization	0.113±0.002	0.090±0.002	0.80±0.03
$[Fe(phen)_3]^{2+}$			
dissociation	0.795±0.016	0.587±0.006	0.74±0.03
racemization	6.7±0.3	5.50±0.27	0.82±0.08

Discussion

*Formation of the 1:1 and 1:*m *Aggregates.* In octanesulfonate- and decanesulfonate-containing systems, the racemization rate of $[Ni(phen)_3]^{2+}$ changed with the alkanesulfonate concentration in a similar way to that of the dissociation rate of $[Fe(phen)_3]^{2+}$. On the other hand, in dodecanesulfonate- and tetradecanesulfonate-containing systems, the features of the rate change were somewhat different between the two complexes (Fig. 1). The results of the analysis (Table 1) showed, however, that the K_1, m, and β'_m values for the $[Ni(phen)_3]^{2+}$–RSO_3^- systems agreed with those previously obtained for the $[Fe(phen)_3]^{2+}$–RSO_3^- systems within the limits of experimental uncertainty, even for the latter systems.⁶⁾ This confirmed that the rate changes of $[Ni(phen)_3]^{2+}$ in the dodecane- and tetradecanesulfonate solutions were also induced by the formation of the 1:1 and 1:m aggregates.

The essential agreements of the values for K_1, m, and β'_m between the two complexes (Table 1) also suggests that the formation of aggregates is not specific for the kind of metal ion in the tris(1,10-phenanthroline)metal chelate, but that hydrophobic interaction is responsible for the aggregate formation, as has been proposed previously.⁶⁾ The energy of hydrophobic interaction between $[Ni(phen)_3]^{2+}$ and RSO_3^- was estimated from the K_1 values (Table 1) to be 1.0±0.1 kJ mol^{-1} per methylene group of the sulfonate ion, a value consistent with that of 0.9±0.1 kJ mol^{-1} obtained for $[Fe(phen)_3]^{2+}$ -RSO_3^- systems.

Rate Constants of $[Ni(phen)_3]^{2+}$ *in the 1:1 and 1:*m *Aggregates. The Mechanism of the Racemization of the Complex*: The rate *vs.* concentration curves for the racemization of $[Ni(phen)_3]^{2+}$ are analogous to those for the dissociation, rather than those for the racemization, of $[Fe(phen)_3]^{2+}$ (Fig. 1). The ratios of the rate constants, k_1/k_0 ($\approx$0.1) and k_m/k_1 ($\approx$9), for the racemization of $[Ni(phen)_3]^{2+}$ (Table 2) were of magnitudes comparable to those ($k_1/k_0 \approx 0.2$ and $k_m/k_1 \approx 10$) for the dissociation of $[Fe(phen)_3]^{2+}$. These observations may reflect the process of racemization-*via*-dissociation for $[Ni(phen)_3]^{2+}$.

While $[Fe(phen)_3]^{2+}$ was shown to dissociate by the aid of nucleophiles including water,¹⁰⁾ the racemization of $[Ni(phen)_3]^{2+}$ was reported to be unaffected by a strong nucleophile such as hydroxide.¹¹⁾ In order to see if water is involved in the rate-determining step of the $[Ni(phen)_3]^{2+}$ racemization, studies were made for the D_2O–H_2O isotope effects of this reaction as well as the dissociation and racemization of $[Fe(phen)_3]^{2+}$. Table 3 shows that the rate in D_2O was about 80% of the rate in H_2O in each case studied. This shows that water is involved in the rate-determining step of each reaction;¹²⁾ thus, our attempt to use the H–D isotope effect for the differentiation of the reaction mechanisms failed. Considering that an intramolecular mechanism has been confirmed for the racemization of $[Fe(phen)_3]^{2+}$,⁷⁾ the participation of water molecules in the rate-determining step of the reaction may indicate that a reorganization of the hydration sphere is necessary even for the intramolecular reaction. The failure in differentiating the mechanism by means of the H–D isotope effect may also be due to the fact that the hydrogen atom of H_2O is not directly concerned with the nucleophilic attack of a water molecule, but is involved in the hydrogen bonding with other water molecules or anions.

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