BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (10), 2672—2673 (1977)

Association Constants of Optically Active $[Co(en)_3]^{3+}$ with (+)-Tartrate and Fumarate Ions Determined from the Kinetic Data of Hydrogen-Deuterium Exchange

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(Received April 25, 1977)

The hydrogen-deuterium exchange rates of Λ- and Δ-$[Co(en)_3]^{3+}$ were measured in D_2O solutions containing (+)-tartrate ions. From the kinetic data, the ion-association constants of the Λ- and Δ-isomers with (+)-tartrate ions were determined to be 40 and 32 ($I=0.1$) respectively. Similar measurements with fumarate resulted in the association constant of 16 ($I=0.1$).

In a previous paper,[1] we preliminarily reported the stereoselective hydrogen-deuterium exchange reaction of Λ- and Δ-$[Co(en)_3]^{3+}$ in D_2O solutions in the presence of (+)-tartrate ions.

The present paper will give a further analysis of the experimental results on the exchange reaction rates, from which the association constants of Λ- and Δ-$[Co(en)_3]^{3+}$ with the (+)-tartrate ion and with the fumarate ion will be derived.

Experimental

$[Co(en)_3]Br_3\cdot H_2O$ was prepared by the usual method and resolved into the optical isomers by using silver (+)- and (−)-tartrate. The Λ- and Δ-$[Co(en)_3]Br_3\cdot H_2O$ obtained showed $[\alpha]_D$ values of +125 ° and −124 ° respectively. (+)-Tartrate buffer solutions of a constant pH value (pH=5.00±0.03)** were prepared by dissolving the acid and its sodium salt at a given ratio in a E. Merck D_2O with an isotopic purity of 99.75%; the concentrations of sodium (+)-tartrate in these buffer solutions ranged from 0.006 to 0.15 M (=mol dm^{-3}). The fumarate buffer solutions (pH=5.33±0.03, 0.025—0.12 M) were similarly prepared.

After the complex had been dissolved in the buffer solutions at a constant concentration (0.03 M), the hydrogen-deuterium exchange rates were measured at 25.0 °C. The first-order rate constants were determined in the way described in a previous paper.[1]

Results and Discussion

Table 1 shows the first-order rate constants, k, of hydrogen-deuterium exchange reactions of Λ- and Δ-$[Co(en)_3]^{3+}$ in the presence of (+)-tartrate and of fumarate. The rate constants decreased with the increase in the (+)-tartrate concentration; the change in the rate constant was greater for Λ-$[Co(en)_3]^{3+}$ than for the Δ-isomer, showing a stereoselectivity between Λ- and Δ-$[Co(en)_3]^{3+}$ in the interaction with (+)-tartrate ions. Fumarate ions had a smaller effect without stereoselectivity. These data were analyzed in order to determine the association constants of Λ- and Δ-$[Co(en)_3]^{3+}$ with (+)-tartrate ions and with fumarate ions on the following assumptions:

Table 1. First-order rate costants of hydrogen-deuterium exchange reactions of Λ- and Δ-$[Co(en)_3]^{3+}$ in D_2O[a)]

[(+)-tartrate]/M[b)]	$10^4\,k/s^{-1}$		[fumarate]/M[c)]	$10^3\,k/s^{-1}$
	Λ	Δ		Λ, Δ
0.00614	13.7	13.9	0.0240	3.05
0.0191	11.3	11.9	0.0248	3.00
0.0254	10.5	10.6	0.0359	2.53
0.0487	7.63	8.23	0.0467	2.38
0.0664	6.02	6.70	0.0700	2.02
0.0988	4.97	5.28	0.1079	1.73
0.1035	4.77	5.17	0.1228	1.51
0.1225	3.93	4.42		
0.1485	2.72	3.28		
0.2045	2.55	3.05		

a) The $[Co(en)_3]^{3+}$ concentration was 0.03 M in all cases. b) pH 5.00±0.03. c) pH 5.33±0.03.

i) There is the ion-association equilibrium:

$$RH^{3+} + B^{2-} \rightleftharpoons RHB^{+}$$

where RH^{3+} and B^{2-} represent the complex cation and the buffer anion respectively. The association constant, K, is given by:

$$K = \frac{[RHB^+]}{[RH^{3+}][B^{2-}]}\,\frac{f_1}{f_3 f_2} = \frac{x}{(c_A-x)(c_B-x)}\,\frac{f_1}{f_3 f_2}, \tag{1}$$

where c_A and c_B are the total concentrations of RH^{3+} and B^{2-} respectively, and x the concentration of the ion-pair, RHB^+, at equilibrium. The f_z ($z=1$, 2, and 3) notation represents the activity coefficient of the ions with the charge of z or $-z$.

ii) The hydrogen-deuterium exchange proceeds in the following steps:

$$RH^{3+} + OD^- \overset{K_{OD}}{\rightleftharpoons} RHOD^{2+}$$

$$K_{OD} = \frac{[RHOD^{2+}]}{[RH^{3+}][OD^-]}\,\frac{f_2}{f_3 f_1}, \tag{2}$$

$$RHOD^{2+} \xrightarrow{k'} R^{2+} + HOD, \tag{3}$$

$$R^{2+} + D_2O \longrightarrow RD^{3+} + OD^-. \tag{4}$$

Step 3 with the rate constant, k', is rate-determining, and Step 4 is very fast. The activity coefficients were assumed to be identical for ions of the same $|z|$ value.

iii) The rate of the hydrogen-deuterium exchange of RHB^+ is very slow compared with that of RH^{3+}.

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** The pH values in this paper are the apparent ones of D_2O solutions measured with an ordinary pH meter. Two relations, pD=pH(apparent)+0.40[2] and $K_{W(D_2O)}=0.160\times K_{W(H_2O)}$,[3] were used for the determination of $[OD^-]f_{OD^-}$.

On these assumptions, the observed exchange rate, first-order in the concentration of the complex, c_A, is related to the rate of Step 3:

$$kc_A = k'[\mathrm{RHOD}^{2+}]. \tag{5}$$

Equations 2 and 5 give:

$$kc_A = k'K_{\mathrm{OD}}[\mathrm{RH}^{3+}]\frac{f_3}{f_2}[\mathrm{OD}^-]f_1. \tag{6}$$

On the other hand, Eq. 1 is transformed to:

$$[\mathrm{RH}^{3+}] = c_A\{1+(c_B-x)\frac{f_3f_2}{f_1}K\}^{-1}. \tag{7}$$

Substituting Eq. 7 into Eq. 6, one obtains:

$$k(f_2/f_3) = k'K_{\mathrm{OD}}[\mathrm{OD}^-]f_1\{1+(c_B-x)\frac{f_3f_2}{f_1}K\}^{-1}, \tag{8}$$

or

$$\log k(f_2/f_3) = \log k_{\mathrm{OD}} + \log([\mathrm{OD}^-]f_1) - \log\{1+(c_B-x)\frac{f_3f_2}{f_1}K\}, \tag{9}$$

where k_{OD} is substituted for $k'K_{\mathrm{OD}}$. Since the values of k_{OD} and $[\mathrm{OD}^-]\,f_1$ (activity of OD^- ions) are constant in the present experiments, a $-\log\,(1+X)$ *vs.* $\log X$ curve will fit the $\log k(f_2/f_3)$ *vs.* $\log\{(c_B-x)(f_3f_2/f_1)\}$ plots of the experimental results. The association constant and the k_{OD} value can be determined from the asymptotes of the curve.

The activity coefficient, f_z, was calculated by using the extended Debye-Hückel equation:

$$\log f_z = -\frac{Az^2\sqrt{I}}{1+Ba\sqrt{I}} + bI, \tag{10}$$

with the values of $a=6$ Å and $b=0.1\,z^2$. The ionic strength (I) ranged from 0.18 to 0.64 for the sample solutions containing (+)-tartrate and from 0.12 to 0.43 for the fumarate solutions. All the kinetic data were corrected to $I=0.1$ by means of Eq. 10.

An approximate K value was obtained from the curve-fitting with the first approximation of $(c_B-x)(f_3f_2/f_1)=c_B(f_3f_2/f_1)$ and $I=6c_A+3c_B$, and was then used to calculate the value of x with Eq. 1. Then, f_1, f_2, and f_3 were recalculated with $I=6c_A+3c_B-6x$. The second curve-fitting for the $\log k(f_2/f_3)$ *vs.* $\log\{(c_B-x)(f_3f_2/f_1)\}$ plots gave a better K value. Further repetition of the procedure reproduced the K value within the limits of experimental error.

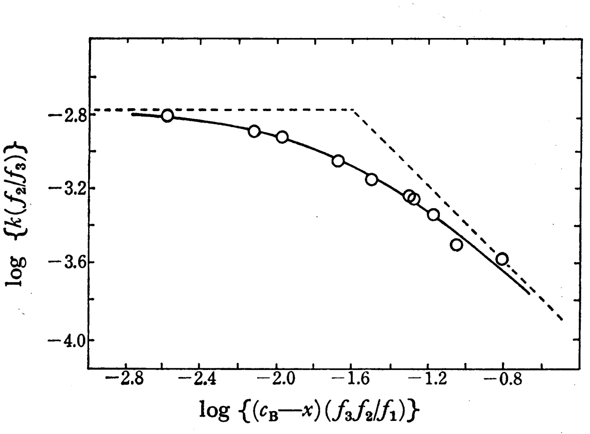

Fig. 1. The curve-fitting for the results on the Λ-[Co(en)$_3$]$^{3+}$-(+)-tartrate(2−) system. ○: Experimental values, ——: the normalized curve, ----: asymptotes for the curve.

TABLE 2. VALUES OF THE ASSOCIATION CONSTANT, K, AND OF THE RATE CONSTANT, k_{OD}, AT 25 °C

Ion-pair	K This work	K Ref. 4$^{a)}$	K Ref. 5$^{b)}$	$10^{-6}\,k_{\mathrm{OD}}/\mathrm{M^{-1}\,s^{-1}}$ This work
Λ + (+)-tart(2−)	40	26±2	55.8±1.4	4.2
Δ + (+)-tart(2−)	32	21±2	50.4±1.8	4.1
$\Lambda(\Delta)$ + fumarate(2−)	16			4.5

a) Measured at $I=0.1$ (adjusted with $\mathrm{NaClO_4}$). b) Corrected to $I=0.1$ using the equation: $\log f_z = -Az^2\sqrt{I}/(1+Ba\sqrt{I})$, with the value of $a=6$Å.

Figure 1 shows a typical example of the curve-fitting for Λ-[Co(en)$_3$]$^{3+}$ after repeated successive approximations as has been described above, while Table 2 summarizes the resulting K and k_{OD} values, together with the literature values. Our K values for the Λ- and Δ-[Co(en)$_3$]$^{3+}$-(+)-tartrate ion-pairs are intermediate between the two sets of literature values[4,5] obtained from spectrophotometric measurements. Yoneda *et al.*[5] have claimed that the smaller K values obtained by Ogino and Saito[4] may be ascribed to the neglect of the association of [Co(en)$_3$]$^{3+}$ with $\mathrm{ClO_4^-}$; the latter authors added $\mathrm{NaClO_4}$ to the sample solutions to adjust the ionic strength. In the present experiments, the sample solutions contained a constant amount of bromide ions derived from $[\mathrm{Co(en)_3}]\mathrm{Br_3 \cdot H_2O}$. Therefore, our K values may be slightly too small because of the neglect of the association of [Co(en)$_3$]$^{3+}$ with $\mathrm{Br^-}$.

The k_{OD} values given in Table 2 can be compared with the value of $2.4\times10^6\ \mathrm{M^{-1}\,s^{-1}}$ obtained by Palmer and Basolo[6] in an acetate buffer solution, considering that different methods were used for the estimation of the $\mathrm{OD^-}$ concentrations. As is shown in Table 2, the K values are about twice as large for (+)-tartrate ions as for fumarate ions. This is consistent with the conclusion from our previous circular-dichroism studies that the (+)-tartrate ion would be favored in the formation of hydrogen bonds through N–H hydrogens of the complex ion.[7]

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