



Kinetics and mechanism of the bicarbonate dehydration of the half-sandwich zinc(II) complexes $[\text{Tp}^{\text{Ph}}]\text{ZnX}$ ($[\text{Tp}^{\text{Ph}}] =$ hydrotris(3-phenylpyrazolyl)borate; $\text{X}^- = \text{OH}^-, \text{N}_3^-, \text{NCS}^-$)

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Abstract

The preparation and characterization of the half-sandwich zinc complexes $[\text{Tp}^{\text{Ph}}]\text{ZnX}$ ($[\text{Tp}^{\text{Ph}}] =$ hydrotris(3-phenylpyrazolyl)borate; $\text{X}^- = \text{OH}^-$ (**1**), N_3^- (**2**), NCS^- (**3**)) have been described. The bicarbonate dehydration kinetic measurements are performed by the stopped-flow techniques at $\text{pH} < 7.9$. The apparent dehydration rate constant $k_{\text{obs}}^{\text{d}}$ varies linearly with the total Zn(II) concentration, and the catalytic activity of the model complexes decreases in the order **1** > **2** > **3**. The catalytic activity decreases with increasing pH, which indicates that the aqua model complex must be the reactive catalytic species in the catalyzed dehydration reaction and the rate-determining step is the substitution of the labile water molecule by HCO_3^- . The $k_{\text{obs}}^{\text{d}}$ values increase with increasing reaction temperature, and the apparent activation energies of the model complexes with small inorganic ions are remarkably higher, this being the origin of inhibition. The large negative entropy of activation also indicates an associative mode of activation in the rate-determining step. The inhibition ability of NCS^- is strong than that of N_3^- , which can be rationalized by the decrease in effective atomic charges of the Zn(II) ions as revealed by the theoretical calculations.

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Keywords: Homogeneous catalysis; Dehydration kinetics; Stopped-flow techniques; Zinc; Inhibitors

1. Introduction

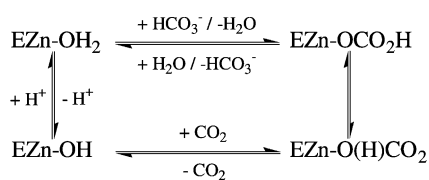
The reversible hydration of CO_2 catalyzed by transition metal complexes plays an important role in biological systems as well as in the industry [1–4].

Carbonic anhydrases (CAs) are zinc-containing proteins that effectively catalyze the reversible hydration of CO_2 . The most widely accepted catalytic cycle for CAs is the so-called zinc-hydroxide mechanism (see Scheme 1, in which E stands for enzyme) [5,6]. The catalytic activity is characterized by $\text{p}K_{\text{a}}$ value of ca. 7.0, such that hydration of CO_2 is dominant above pH 7, while dehydration of HCO_3^- is observed below pH 7. It has been postulated that this $\text{p}K_{\text{a}}$ value represents that of the coordinated water molecule on the Zn(II) ion center. The catalytic activities of bicarbonate

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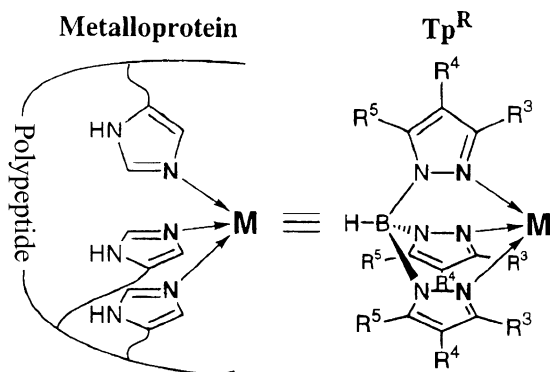
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Scheme 1.

dehydration are greatly held back in the presence of inhibitors, most of which are small inorganic anions (e.g. NCS^- , N_3^- , I^- , NO_2^-) [7,8]. Despite of the numerous papers in recent years focusing on the kinetic study of bicarbonate dehydration catalyzed by transition metal complexes [9–12], studies concerning the role of inhibitors during the dehydration of HCO_3^- are relatively few [13–15].

We have performed kinetic measurement and mechanistic study of a series of half-sandwich zinc(II) complexes $[\text{Tp}^{\text{Ph}}]\text{ZnX}$ ($[\text{Tp}^{\text{Ph}}]$ = hydrotris(3-phenylpyrazolyl)borate; $\text{X}^- = \text{OH}^-$ (1), N_3^- (2), NCS^- (3)). Our intention in this present contribution is two-fold: (1) the elucidation of the origin of inhibition by the detailed study on the effects of inhibitors on the dehydration of HCO_3^- ; (2) the rationalization of the variations in inhibition ability between two different small inorganic ions. Trofimenko's hydrotris(pyrazolyl)borate ligand system $[\text{Tp}^{\text{R}}]$ has been applied to synthesize these complexes [16,17], since it is advantageous to mimic the coordination environment of CAs by using the trigonally capping Tp^{R} ligand system (Scheme 2).



Scheme 2.

2. Experimental

2.1. Instrumentation

Elemental analyses for C, H, and N were carried out on a Perkin-Elmer analyzer at the Institute of Elemento-Organic Chemistry, Nankai University. Infrared spectra on KBr pellets were recorded on a Shimadzu IR-408 spectrophotometer in the range of $4000\text{--}600\text{ cm}^{-1}$. UV-Vis spectra in methanol were recorded on a Shimadzu UV-2101 spectrophotometer in the range of $1000\text{--}200\text{ nm}$. Mass spectrum was performed at the Central Laboratory of Nankai University on VG ZAB-HS spectrometer.

2.2. Materials and methods

All the starting chemicals used in this work were of analytical reagent and used without further purification, unless otherwise stated. Potassium hydrotris(3-phenylpyrazolyl)borate was synthesized according to the literature method [18], and the purity was confirmed by IR, MS-FAB, and elemental analysis. The indicator bromocresol purple (Sigma) and the biological buffer Tris (tris(hydroxymethyl)aminomethane, Sigma) were purchased and used as received. All solutions were prepared using double distilled water that was boiled for more than 2 h prior to use to remove the dissolved CO_2 . The concentrations of the indicator, Tris, and NaClO_4 were kept at 2.5×10^{-4} , 7.0×10^{-2} , and $7.5 \times 10^{-2}\text{ M}$, respectively.

2.3. Synthetic procedures

Caution! The perchlorate salts in this study are all potentially explosive and should be handled with care. The complex $[\text{Tp}^{\text{Ph}}]\text{ZnOH}$ (1) was synthesized as follows: $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.745 g, 0.2 mmol) in 5 ml of methanol was added dropwise to 10 ml of methanol containing $\text{K}[\text{Tp}^{\text{Ph}}]$ (0.959 g, 0.2 mmol). The mixture was stirred at room temperature for 2 h. Then, the pH value of the above mixture was adjusted to ca. 8 by adding KOH (1 M), and stirred for another 10 h. White microcrystals for 1 were obtained and recrystallized from methanol (0.869 g, yield 83%). The complex $[\text{Tp}^{\text{Ph}}]\text{ZnN}_3$ (2) was synthesized by adding $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.745 g, 0.2 mmol) in 5 ml

of methanol dropwise to 10 ml of methanol containing $K[TP^{Ph}]$ (0.959 g, 0.2 mmol). The mixture was stirred at room temperature for 10 h. Then, NaN_3 (0.039 g, 0.6 mmol) dissolved in the minimum water was added to the above mixture, and stirred for another 10 h (0.878 g, yield 80%). The same procedure used for **2** was employed to synthesize $[TP^{Ph}]ZnNCS$ (**3**). From $Zn(ClO_4)_2 \cdot 6H_2O$ (0.745 g, 0.2 mmol), $K[TP^{Ph}]$ (0.959 g, 0.2 mmol) and $KSCN$ (0.058 g, 0.6 mmol) was obtained **3** (1.016 g, yield 90%). Anal. for **1**, calcd. for $C_{27}H_{23}BN_6OZn$: C, 61.95; H, 4.39; N, 16.05. Found C, 61.82; H, 4.53; N, 15.93. IR (KBr) 2500 (B–H), 3620 (O–H) cm^{-1} . Anal. for **2**, calcd. for $C_{27}H_{22}BN_9Zn$: C, 59.12; H, 4.01; N, 22.97. Found C, 58.95; H, 4.10; N, 22.82. IR (KBr) 2505 (B–H), 2090 (N≡N) cm^{-1} . Anal. for **3**, calcd. for $C_{28}H_{22}BN_7SZn$: C, 59.58; H, 3.90; N, 17.36. Found C, 59.40; H, 4.02; N, 17.24. IR (KBr) 2495 (B–H), 2085 (C≡N) cm^{-1} .

2.4. Kinetic measurements

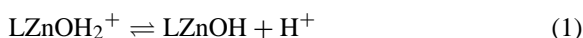
All kinetic measurements in 70% ethanol/ H_2O (v/v) mixed solution were made with a Union Giken RA-401 stopped-flow spectrophotometer equipped with a Union Giken RA-451 rapid-scan attachment in order to determine the change in absorption of the reaction mixture directly after mixing under a certain light wavelength. Temperature was maintained by using a Union Giken RA-454 superthermostat, and temperature accuracy is within 0.1 K. The pH values in this work were all directly measured by means of a Beckman Φ 71 pH meter. The ionic strength of all test solutions was adjusted to 0.11 M with the aid of $NaClO_4$ for the dehydration reaction. HCO_3^- solutions (7.5×10^{-3} M) were freshly prepared from $NaHCO_3$ and used within 10 h. The most appropriate pH value and light wavelength to study the reaction for this buffer–indicator pair (Tris with bromocresol purple) are ca. 7.0 and 595 nm, respectively, which are revealed by UV-Vis absorption spectra. Therefore, the reaction is monitored at 595 nm wavelength with a tungsten lamp as the light source. The apparent first-order dehydration rate constants (k_{obs}^d) were obtained with at least three half-lives and represent the average of the best three runs. Reproducibility of the values of k_{obs}^d was better than $\pm 5\%$.

2.5. Theoretical calculations

During the dehydration process of HCO_3^- , the nucleophilic attack of the free HCO_3^- on the Zn(II) ion of the model complex is affected by the effective atomic charge of the Zn(II) ion. To obtain information on the variations in the effective atomic charge of the Zn(II) ion by coordinating different inhibitors (N_3^-/NCS^-), we have carried out theoretical calculations of **2** and **3** at the HF/lanl2dz level. This basis set consisted of the 6-31G** basis functions for H, B, C, N, O, and S [19] and the Los Alamos effective core potential (ECP) for Zn with the outermost core orbitals included in the valence description [20–22]. Since zinc(II) ion has a d^{10} electronic configuration, the type of closed shell calculation has been used here. All calculations were carried out using the Gaussian-98 package [23].

3. Results and discussion

The kinetics of the dehydration reaction in ethanol/ H_2O mixed solution was followed by the determination of the changes in absorption spectra as a function of time when HCO_3^- was added to the reaction mixture, whereas the hydrogen ion concentration was maintained constant by means of buffer solutions. A first-order reaction with respect to the concentration of Zn(II) complex was observed in all the cases. That is, the dehydration kinetics of HCO_3^- follow the rate law $V^d = k_{obs}^d C_{com}$, where k_{obs}^d is the apparent first-order dehydration rate constant, and C_{com} is the total concentration of the complex. The catalytic activity of model complexes is characterized by pK_a value. The dehydration kinetic measurements of HCO_3^- should be carried out in the case of $pH < pK_a$ to avoid the interference of the reverse hydration reaction especially at higher pH. pH titration of the model complexes were performed in the pH range 6–8, which established that two species $LZnOH_2^+$ and $LZnOH$ are formed as given in (1) (L: ligand).



The pK_a values are found to be around 7.9 for the above compounds, but not the same as each other. In order to understand the effects of small inorganic

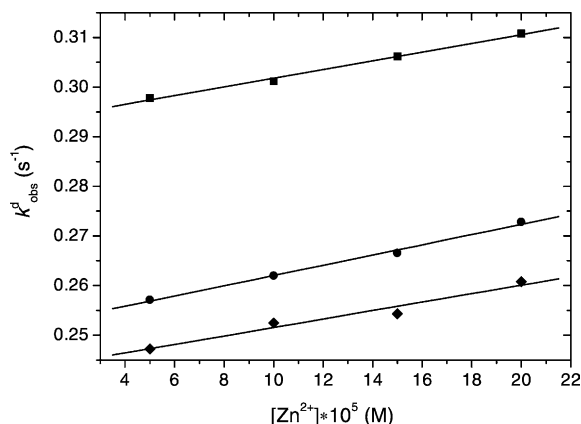
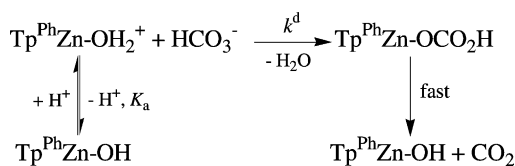


Fig. 1. Plot of $k_{\text{obs}}^{\text{d}}$ vs. $[\text{Zn}^{2+}]$ for the dehydration of HCO_3^- . Experimental conditions: pH 7.014; $[\text{NaHCO}_3] = 7.5 \times 10^{-3} \text{ M}$; ionic strength = 0.11 M; [buffer] = $7.0 \times 10^{-2} \text{ M}$; [indicator] = $2.5 \times 10^{-4} \text{ M}$; temperature = 25.0 °C. Key: (■) 1; (●) 2; (◆) 3.

ions on the dehydration of HCO_3^- , the apparent dehydration rate constant $k_{\text{obs}}^{\text{d}}$ of the model complexes in the absence/presence of inhibitors are measured at the following four aspects: concentration of the model complexes, pH value, free inhibitors, and temperature.

3.1. Concentration of the model complexes

Typical kinetic traces observed for different concentrations of the Zn(II) complexes catalyzed dehydration of HCO_3^- at pH 7.014 (≈ 7.0 , the most appropriate pH value to study the reaction as denoted in the Section 2) are shown by the plot of $k_{\text{obs}}^{\text{d}}$ versus $[\text{Zn}^{2+}]$ in Fig. 1 (Zn^{2+} = zinc(II) complex). It is evident that the apparent dehydration rate constant $k_{\text{obs}}^{\text{d}}$ varies linearly with total Zn(II) concentration. However, the dehydration reaction is only slightly catalyzed by the Zn(II) complexes. Hence, a typical catalyst concentration of $1.5 \times 10^{-4} \text{ M}$ is selected and used in the following measurements. The catalytic activity of the model complexes decreases in the order $1 > 2 > 3$, which shows that the dehydration process is affected by the Zn(II) complexes in the presence of inhibitors. The effect of free Zn(II) ions on the reaction was also checked at the same pH value, but no catalysis was observed.



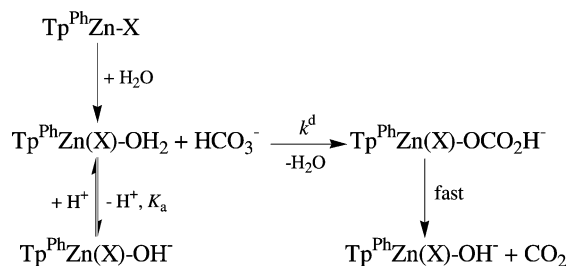
Scheme 3.

3.2. pH value

To examine the effects of pH value on the catalytic reactions, the dehydration kinetics of HCO_3^- catalyzed by the model complexes were then studied in the pH range 7.0–7.9 under the same experimental conditions. The pH range was once again restricted by the interference of the hydration reaction of CO_2 at higher pH. The pH dependence of $k_{\text{obs}}^{\text{d}}$ can be account for in terms of the mechanisms I and II outlined in Schemes 3 and 4, respectively, which are based on the principle that only the aqua complex can react with HCO_3^- in order to catalyze the dehydration reaction ($\text{X}^- = \text{N}_3^-/\text{NCS}^-$) [33]. In these two mechanisms it is assumed that the produced bicarbonate complex is unstable and rapidly releases CO_2 . It is reasonable to assume that no stable bicarbonate complex is formed since the release of CO_2 was observed during the reaction. In addition, no evidence whatsoever could be found for the presence of such a complex. Therefore, the rate-determining step of the dehydration reaction must be the substitution of the labile water molecule by HCO_3^- , which nucleophilic attacks on the Zn(II) ion of the model complex.

As have been pointed out, the observed reaction rate is of first-order with respect to the total complex concentration C_{com}

$$V^{\text{d}} = k_{\text{obs}}^{\text{d}} C_{\text{com}} \quad (2)$$



Scheme 4.

From the following stoichiometric equation (L = ligand)



we have

$$C_{\text{com}} = [\text{LZnOH}_2^+] \left[\frac{1 + K_a}{[\text{H}^+]} \right] \quad (4)$$

According to the above proposed mechanisms,

$$V^{\text{d}} = k^{\text{d}}[\text{LZnOH}_2^+] = k^{\text{d}}C_{\text{com}} \frac{[\text{H}^+]}{([\text{H}^+] + K_a)} \quad (5)$$

therefore

$$k_{\text{obs}}^{\text{d}} = \frac{k^{\text{d}}[\text{H}^+]}{([\text{H}^+] + K_a)} \quad (6)$$

The kinetic data were thus fitted to the suggested mechanisms I and II, for which the corresponding rate law is given in (6). Accordingly, a plot of $(k_{\text{obs}}^{\text{d}})^{-1}$ versus $[\text{H}^+]^{-1}$ should be linear, which is the case for the experimental data (see Fig. 2). It is evident from the figure that the catalytic activity decreases with increasing pH and the catalytic activity of the model complexes decreases in the same order, which is consistent with the above measurements. This trend suggests that the aqua complex must play a crucial role in the catalyzed dehydration of HCO_3^- , similar to that

Table 1

The calculated k^{d} , K_a , and $\text{p}K_a$ values of the model complexes^a

Model Complex	k^{d} (s^{-1})	K_a (M) ($\times 10^{-8}$)	$\text{p}K_a$
1	0.335	1.23	7.91
2	0.303	1.55	7.81
3	0.287	1.55	7.81

^a Experimental conditions: $[\text{NaHCO}_3] = 7.5 \times 10^{-3}$ M; $[\text{Zn}^{2+}] = 1.5 \times 10^{-4}$ M; ionic strength = 0.11 M; [buffer] = 7.0×10^{-2} M; [indicator] = 2.5×10^{-4} M; temperature = 25.0°C .

reported in the literature [9,24]. From fitting of the experimental points using the Eq. (6), we can obtain the dehydration rate constant of the rate-determining step k^{d} , acid dissociation constant K_a , and corresponding $\text{p}K_a$ values of the model complexes, which are listed in Table 1. The latter values are rather close to that found from the pH titrations of the catalyzed dehydration reaction of HCO_3^- when the limited pH range is taken into account, and underlines the validity of suggested mechanisms. Again, it was checked that the free Zn(II) ions had no effect on the reaction, so that the observed catalytic effect must be due to the model complexes.

3.3. Free inhibitors

To further confirm the mechanism II and have a better understanding of the effects of small inorganic ions on the dehydration reaction, we also measured the dehydration kinetics of HCO_3^- catalyzed by the model complex 1 in different $[\text{X}^-]/[\text{Zn}^{2+}]$ molar ratios (X^- = free inhibitor $\text{N}_3^-/\text{NCS}^-$; Zn^{2+} = zinc(II) complex). Fig. 3 shows the plot of $k_{\text{obs}}^{\text{d}}$ versus $[\text{X}^-]/[\text{Zn}^{2+}]$ for the dehydration of HCO_3^- catalyzed by 1. Seen from the figure, the catalytic activity decreases with increasing molar ratios of $[\text{X}^-]/[\text{Zn}^{2+}]$ from 0 to 10, and the inhibition ability decreases in the order: $\text{NCS}^- > \text{N}_3^-$. What should be mentioned is that in the case of $[\text{X}^-]/[\text{Zn}^{2+}] = 1$, $k_{\text{obs}}^{\text{d}}$ values observed here are almost the same as those of 2 and 3, respectively, at the same pH as shown in Fig. 2. When the molar ratios of $[\text{X}^-]/[\text{Zn}^{2+}] > 1$, no marked change in $k_{\text{obs}}^{\text{d}}$ is observed. The results here indicate that before the dehydration of HCO_3^- catalyzed by the model complex 1 the free inhibitor coordinates to the Zn(II) ion forming a five-coordinated adduct, and the

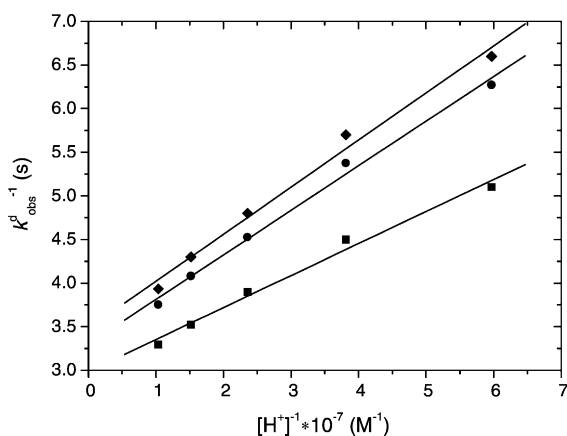


Fig. 2. Plot of $(k_{\text{obs}}^{\text{d}})^{-1}$ vs. $[\text{H}^+]^{-1}$ for the dehydration of HCO_3^- . Experimental conditions: $[\text{NaHCO}_3] = 7.5 \times 10^{-3}$ M; $[\text{Zn}^{2+}] = 1.5 \times 10^{-4}$ M; ionic strength = 0.11 M; [buffer] = 7.0×10^{-2} M; [indicator] = 2.5×10^{-4} M; temperature = 25.0°C . Key: (■) 1; (●) 2; (◆) 3. The solid line was calculated on the basis of the mechanisms outlined in Eq. (6) (see Section 3).

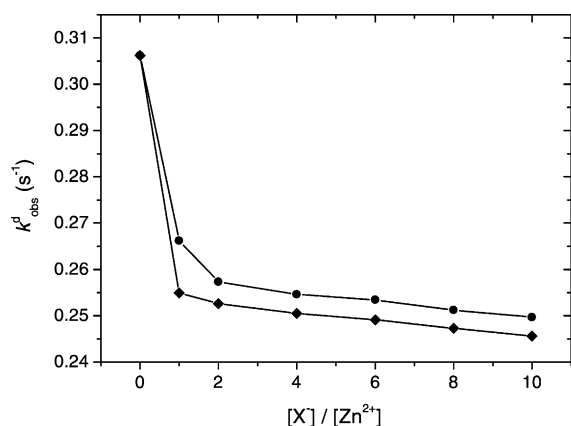
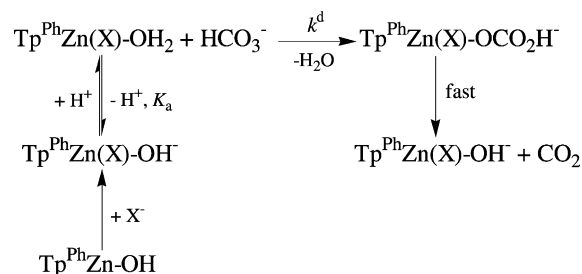


Fig. 3. Plot of $k_{\text{obs}}^{\text{d}}$ vs. $[X^-]/[Zn^{2+}]$ for the dehydration of HCO_3^- catalyzed by **1**. Experimental conditions: pH 7.014; $[\text{NaHCO}_3] = 7.5 \times 10^{-3} \text{ M}$; $[\text{Zn}^{2+}] = 1.5 \times 10^{-4} \text{ M}$; ionic strength = 0.11 M; [buffer] = $7.0 \times 10^{-2} \text{ M}$; [indicator] = $2.5 \times 10^{-4} \text{ M}$; temperature = 25.0°C . Key: (●) $X^- = \text{N}_3^-$; (◆) $X^- = \text{NCS}^-$.

remaining uncoordinated inhibitors have little effect on the dehydration reaction. Based on these analyses, we present the mechanism III interpreting the effects of free inorganic ions on the dehydration of HCO_3^- catalyzed by the model complex **1** (Scheme 5). It is easy to note that the catalytic process outlined in mechanism III is in connection with mechanism II, the five-coordinated aqua model complex being the reactive catalytic species in both mechanisms.

3.4. Temperature

The activation parameters for the dehydration reaction were determined from the temperature dependence of the $k_{\text{obs}}^{\text{d}}$ values. The temperature dependent



Scheme 5.

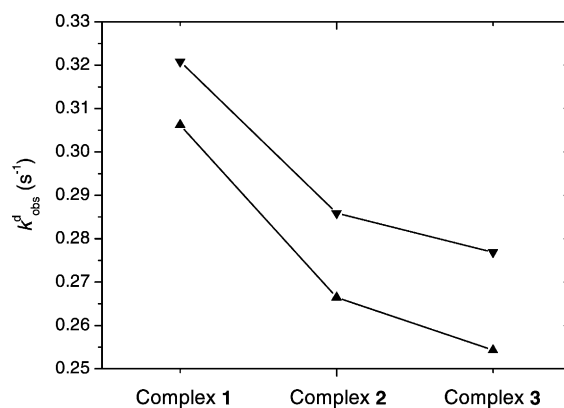


Fig. 4. Plot of $k_{\text{obs}}^{\text{d}}$ vs. the model complexes for the dehydration of HCO_3^- at 298 and 310 K, respectively. Experimental conditions: pH 7.014; $[\text{NaHCO}_3] = 7.5 \times 10^{-3} \text{ M}$; $[\text{Zn}^{2+}] = 1.5 \times 10^{-4} \text{ M}$; ionic strength = 0.11 M; [buffer] = $7.0 \times 10^{-2} \text{ M}$; [indicator] = $2.5 \times 10^{-4} \text{ M}$. Key: (▼) 310 K; (▲) 298 K.

dehydration reaction rate constants are measured at 298 and 310 K, respectively. Plot of $k_{\text{obs}}^{\text{d}}$ versus different model complexes for the catalyzed dehydration of HCO_3^- at 298 and 310 K, respectively, is shown in Fig. 4. The measurement results show that the $k_{\text{obs}}^{\text{d}}$ values increase with increasing reaction temperature, which is consistent with the enzyme catalytic behavior. From the Eyring Eq. (7) and Arrhenius Eq. (8)

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H_m^\ddagger}{RT} + \frac{\Delta S_m^\ddagger}{R} + \ln\left(\frac{R}{N_a h}\right) \quad (7)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a(T_2 - T_1)}{RT_1 T_2} \quad (8)$$

where the symbols have their usual meanings, the activation parameters of the rate-determining step can be obtained from the corresponding k^{d} values. The activation enthalpy ΔH_m^\ddagger , activation entropy ΔS_m^\ddagger , and apparent activation energy E_a are given in Table 2. Although the activation parameters are often not discriminating factors in recognizing the reaction pathway, the large negative entropy of activation (ΔS_m^\ddagger), however, clearly indicates an associative mode of activation in the rate-determining step. This step can be assigned to the reaction between the aqua model complex and HCO_3^- , which is consistent with our proposed dehydration mechanisms. The apparent activation energies of the model complexes **2** ($4.506 \text{ kJ mol}^{-1}$) and

Table 2

The activation parameters ΔH_m^\ddagger , ΔS_m^\ddagger , and E_a of the rate-determining step^a

Model complex	ΔH_m^\ddagger (kJ mol ⁻¹)	ΔS_m^\ddagger (JK ⁻¹ mol ⁻¹) ($\times 10^2$)	E_a (kJ mol ⁻¹)
1	0.459	-3.257	2.986
2	1.979	-3.214	4.506
3	2.921	-3.187	5.448

^a Experimental conditions: pH 7.014; [NaHCO₃] = 7.5 $\times 10^{-3}$ M; [Zn²⁺] = 1.5 $\times 10^{-4}$ M; ionic strength = 0.11 M; [buffer] = 7.0 $\times 10^{-2}$ M; [indicator] = 2.5 $\times 10^{-4}$ M.

3 (5.448 kJ mol⁻¹) are remarkably higher than that of **1** (2.986 kJ mol⁻¹), this being the origin of inhibition that the dehydration reaction of HCO₃⁻ catalyzed by the model complex is held back by inhibitors.

In general, the catalytic activity of the model complexes in our kinetic measurements is characterized by pK_a value of 7.9 and therefore the model complexes exhibit a catalytic activity for the dehydration of HCO₃⁻ at pH < 7.9. It is easy to note that our proposed mechanism I is well in agreement with the so-called zinc-hydroxide mechanism for CAs. The reactive catalytic species in both of these mechanisms show a tetrahedral geometry of the Zn(II) ion with a N₃O donor set.

Moreover, the mechanisms I and II are quite similar, i.e. the dehydration processes of HCO₃⁻ catalyzed by the model complexes in the absence and presence of inhibitors are comparable with each other. Therefore, the overall mechanism of dehydration of HCO₃⁻ catalyzed by the model complexes can be stated as follows: in the case of pH < pK_a, the aqua model complex exhibits the catalytic activity on the dehydration of HCO₃⁻ in which the rate-determining step is the substitution of the labile water molecule by HCO₃⁻, followed by the rapid decarboxylation of the coordinated bicarbonate molecule as found for many model bicarbonate complexes. Despite of the similar catalytic process outlined in these two mechanisms, a solvent water molecule coordinates to the Zn(II) ions of **2** and **3**, respectively, to complete a five-coordinated aqua model complex showing a trigonal bipyramidal coordination geometry. This five-coordinated inhibitor adduct is considered as the reactive catalytic species in the dehydration of HCO₃⁻, which is also confirmed by the mechanism III. It is evident from the latter two mechanisms that the inhibitor does not indeed involve in

the catalytic process. However, remarkable inhibition was observed that $k_{\text{obs}}^{\text{d}}$ of the model complexes **2** and **3** are significantly smaller than that of **1**. That is, dehydration of HCO₃⁻ catalyzed by the model complexes with coordinated inorganic ions leads to higher activation energy barriers, as verified by the kinetic measurements. The higher activation energy must be the origin of inhibition that the dehydration reaction catalyzed by the model complexes is held back by N₃⁻ and NCS⁻.

It is evident from the experimental measurements that the inhibition ability of NCS⁻ is stronger than that of N₃⁻. During the dehydration process of HCO₃⁻, the nucleophilic attack of the free HCO₃⁻ on the Zn(II) ion of the model complex is affected by the effective atomic charge of the Zn(II) ion. In this case, the nitrogen atom of the inorganic ion (N₃⁻/NCS⁻) that coordinates to the Zn(II) ion serves as the electron donor. Low effective atomic charges caused by stronger donor inhibitors is disadvantageous to the nucleophilic attack of the free HCO₃⁻ ion on the Zn(II) ion. To obtain information on the variations in the effective atomic charge of the Zn(II) ion by coordinating different inorganic ions (N₃⁻/NCS⁻), we have carried out theoretical calculations of **2** and **3** at the HF/lanl2dz level, in which the type of close shell calculation has been used. From the Gaussian output files, the values have been found to be 1.367 and 1.354 for the Zn(II) ions of **2** and **3**, respectively. Therefore, we can conclude that the electrons from the N donor atom of NCS⁻ are more delocalized on the Zn(II) ion leading to the decrease of the effective atomic charge of the Zn(II) ion, which can rationalize the variations in inhibition ability between N₃⁻ and NCS⁻.

4. Conclusions

In summary, we have performed here the detailed kinetic study on the dehydration of HCO₃⁻ catalyzed by a series of half-sandwich zinc(II) complexes [Tp^{Ph}]ZnX. The apparent dehydration rate constant $k_{\text{obs}}^{\text{d}}$ of **2** and **3** is markedly lower than that of **1**, as shown at four aspects:

- (1) Concentration of the model complexes: the apparent dehydration rate constant $k_{\text{obs}}^{\text{d}}$ varies linearly with total Zn(II) concentration, and the catalytic activity of the model complexes decreases in the order **1** > **2** > **3**.

- (2) pH value: the catalytic activity decreases with increasing pH indicating that the aqua model complex must be the reactive catalytic species in the catalyzed dehydration reaction and the rate-determining step is the substitution of the labile water molecule by HCO_3^- . The coordination spheres of the aqua model complexes in the absence and presence of inhibitors are four-coordinated tetrahedron and five-coordinated trigonal bipyramid, respectively.
- (3) Free inhibitors: the free inhibitor coordinates to the Zn(II) ion of **1** forming a five-coordinated adduct before the dehydration of HCO_3^- is catalyzed by the model complex **1**, and the remaining uncoordinated inhibitors have little effect on the dehydration reaction.
- (4) Temperature: the $k_{\text{obs}}^{\text{d}}$ values increase with increasing reaction temperature, and the apparent activation energies of the model complexes with inhibitors are remarkably higher. The large negative entropy of activation indicates an associative mode of activation in the rate-determining step.

In all, the dehydration reaction of HCO_3^- catalyzed by the model complexes is held back by small inorganic ions, which leads to a higher activation barrier being the origin of inhibition. In particular, the inhibition ability of NCS^- is stronger than that of N_3^- , which can be rationalized by the decrease in the effective atomic charges of the Zn(II) ions as revealed by the theoretical calculations in this work. Further work on the bicarbonate dehydration kinetics catalyzed by other transition metal complexes using Tp^{R} ligand system is under way in our laboratories.

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