Inorganica Chimica Acta, 130 (1987) 157–162

Kinetics of Acid-catalysed Dissociation of Lead(II) and Copper(II) Complexes of Ethylenebis(oxyethylenenitrilo)tetraacetic Acid (EGTA)

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(Received August 11, 1986)

Abstract

The acid-catalysed dissociation rate constants for $PbEGTA^{2-}$ and $CuEGTA^{2-}$ complexes (where EGTA is ethylenebis(oxyethylenenitrilo)tetraacetic acid) were measured in acetic acid–acetate buffer medium (pH: 3.9–4.8) and perchloric acid solutions ($[H^+]$ = 0.05–0.15 M), respectively, at a constant ionic strength of 0.15 ($NaClO_4$). The rate laws shown by the lead(II) and copper(II) complexes are of the form, Rate = $\{k_d + k_H[H^+]\}$[complex] and Rate = $\{k_d + k_{H^2}[H^+]^2\}$[complex], respectively. The enthalpy and entropy of activation for acid-independent and acid-catalysed pathways for both the complexes were obtained by the temperature-dependence studies of resolved rate constants in the 16–45 °C range. The rate of dissociation of $PbEGTA^{2-}$ is not enhanced by increasing the concentration of acetate ion in the buffer, and the amount of total electrolyte in the reaction mixture has no pronounced effect on the dissociation rates of either the lead(II) or copper(II) complex. Attempts to study the kinetics of stepwise ligand unwrapping in the binuclear Cu_2-EGTA complex were unsuccessful due to the extremely rapid dissociation of this complex to yield mononuclear $CuEGTA^{2-}$.

Introduction

The kinetics and reaction mechanisms of metal complexes containing polydentate ligands have been the subject of continuing interest [1, 2], as evidenced by several books [3–5] and a number of review articles [6–8] which have appeared in recent years dealing with this topic. Such studies are important not only from the point of view of the coordination chemistry of metal ions but also because of the valuable information they furnish regarding the strength and nature of interactions of metal ions with biologically important ligands *viz.* peptides, proteins, nucleic acids, amino acids and vitamins. The rates of dissociation of these complexes have implications in analytical chemistry also, as they provide the information regarding the life-times of such complexes in the presence of several ions in solution at different pH levels and temperatures, which helps to improve the existing methods of metal ion separations such as ion-exchange chromatography and solvent extraction.

The dissociation mechanism for metal complexes seems to vary from complex to complex, but some generalities can be drawn in terms of available pathways. Most complexes with mono- and polydentate ligands do exhibit acid-independent and acid-dependent pathways in aqueous solution [9, 10], the former being assisted by the solvent. The presence of acid in the reaction mixture can have a profound influence on the rates of complex dissociation. Acid-catalysed reactions are feasible for complexes which contain a basic ligand and their rates show a strong pH dependence. Rate acceleration in the presence of acid [11] can occur in two possible ways. (i) After the bond between the metal ion and ligating atom is broken, the reformation or the ring-closing in the case of chelating ligands could be prevented by protonation of the free coordinating atoms. Such a process can be detected by following the variations in observed rate constants, with increase in acid concentration, as this reaction is expected to become zero-order in acid at high acid concentrations [11]. (ii) By breaking the metal–ligand bonds resulting from direct electrophilic attack of the acid on coordinated atoms such as amino nitrogen(s) or carboxylate oxygen(s). This reaction is either first-order or higher order in acid and can show strong steric effects due to its associative nature [6].

Recently we have embarked upon a systematic and detailed investigation of the kinetics and reaction mechanism of metal complexes which contain macrocyclic and open-chain polyaminopolycarboxylic acids as ligands, and as a part of this study we made rate measurements on the acid-catalysed dissociation of $PbEGTA^{2-}$ and $CuEGTA^{2-}$ complexes. The results obtained during the course of this investigation are discussed here.

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Experimental

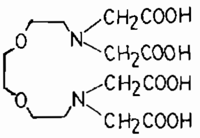
Reagent grade EGTA was obtained in acid form from Aldrich and was used as received. $NaClO_4$ (Aldrich), $(CH_3)_4NOH$ (Aldrich), $Pb(NO_3)_2$ (Aldrich), NaOH (Fisher), CH_3COONa (Fisher), CH_3COOH (MCB), $Cu(NO_3)_2 \cdot 3H_2O$ (MCB), and potassium hydrogen phthalate (MCB) used were of reagent grade and no further purification of these chemicals was performed. All solutions were made in boiled deionised water. Routine absorption spectra of complex, ligand and metal salt solutions were recorded on a Cary 118 (Varian Instruments) spectrophotometer. pH measurements were done on a Fisher Acument Selective Ion Analyser (Model 750) in conjunction with a Fisher combination electrode. The ionic strength was adjusted to 0.15 with $NaClO_4$. Complex solutions were made *in situ* by mixing appropriate amounts of stock solutions of Cu^{2+} or Pb^{2+} and EGTA and adjusting the pH to about 6. The complex concentration in the reaction mixture was maintained at 2.0×10^{-4} M. The buffer solutions were made using a constant concentration of sodium acetate (0.01 M) and varying the amount of acetic acid. The acetate ion concentration in the reaction mixtures is 5.0×10^{-3} unless specified otherwise. The hydrogen ion concentration in the buffer solutions was calculated from the expression $-\log[H^+] = pH + \log f_{H^+}$, after measuring the pH of solutions obtained by mixing equal volumes of complex and buffer solutions.

Kinetic runs were performed on a Durrum-Dionex stopped-flow spectrophotometer as described in our earlier communication [12]. Rates of reactions were monitored by following the decrease in absorbance due to the complex at 253 and 291 nm for $PbEGTA^{2-}$ and $CuEGTA^{2-}$, respectively. Reactions were generally followed up to 3–4 half-lives and 200 data points (absorbance readings) were collected during the course of the reaction. Final absorbance readings (A_∞) were recorded after ten to twelve half-lives of reaction. Excellent straight line plots of $\log(A_t - A_\infty)$ *versus* time (where A_t is absorbance at time t) were obtained for at least three half-lives of reaction. Pseudo-first-order rate constants were calculated from linear and non-linear regression analysis of experimental data after each run. Rate constants (quoted in Tables I and II) represent average values of four measurements or more, and their reproducibility is within ±5% or better. Acid-independent and acid-dependent rate constants were obtained from the least-squares intercept and slope of the linear plots as described in 'Results and Discussion'. The activation parameters for both dissociation paths were determined from Eyring plots in the range of 16–45 °C for Cu(II) complex and 16–35 °C for Pb(II) complex of EGTA.

Results and Discussion

EGTA (Fig. 1) has eight possible coordination sites, *i.e.*, two amino nitrogens, four carboxylate oxygens and two ethereal oxygens. As the maximum coordination number of Cu(II) is believed to be six, one would expect that the amino and carboxylate groups are involved in coordination in $CuEGTA^{2-}$, as the ethereal oxygens (in non-cyclic systems) are not known to bind well to metal ions especially in aqueous solutions. Indirect evidence for the above argument comes from the stability constant data [13] of Cu(II) complexes of EDTA and EGTA. The $\log K$ values are 18.7 and 17.6, respectively at 25 °C and 0.1 ionic strength, which are indicative of a similar environment around the metal ion. Unfortunately the crystal structure of $CuEGTA^{2-}$ is not yet known. Lead(II) ion is known to form a complex with a coordination number of more than six and it may call upon all the available coordination sites in EGTA. It is anticipated that the dissociation mechanisms of these EGTA complexes may parallel that of their EDTA analogues.

The acid-catalysed dissociation rates have been measured for both Pb(II) and Cu(II) complexes of EGTA under pseudo-first-order conditions. The observed rate constants obtained for both Pb(II) and Cu(II) complexes of EGTA, along with the acid concentrations used and the temperatures at which these reactions were done, are listed in Tables I and II, respectively.



EGTA

Fig. 1. Structural formula of EGTA, ethylenebis(oxyethylenenitrilo)tetraacetic acid.

Dissociation Kinetics of $PbEGTA^{2-}$

The observed rate constants (k_{obs}) for the Pb(II) complex increase linearly with increase in acid concentration, which is characteristic of a reaction that is first-order in $[H^+]$. When these rate constants are plotted against $[H^+]$ (Fig. 2), a straight line with a non-zero intercept has been obtained, which corresponds to the rate constant for an acid-independent pathway. The slope of this line gives the rate constant for an acid-catalysed pathway. The self-dissociation rate constant or acid-independent rate constant (k_d) and the rate constant for acid-catalysis (k_H) at each temperature have been resolved by a weighted linear least-squares programme assuming a constant percentage error in observed rate constants, and are presented in Table III as a function of temperature.

TABLE I. Effect of [H^+] on Dissociation Kinetics^a of $PbEGTA^{2-}$

Temperature (°C)	k_{obs} (s^{-1}) at different [H^+] ($10^5[H^+]$ (M))					
	1.55	2.95	4.39	6.01	9.42	12.5
16	7.51	9.63	11.9	14.2	18.9	23.0
25	17.3	21.2	24.9	28.5	36.2	44.4
35	33.8	42.1	50.4	57.0	72.4	91.1

$^a[PbEGTA^{2-}] = 2.0 \times 10^{-4}$ M, $\mu = 0.15$ ($NaClO_4$), [acetate] $= 5.0 \times 10^{-3}$ M.

TABLE II. Effect of [H^+] on Dissociation Kinetics^a of $CuEGTA^{2-}$

Temperature (°C)	k_{obs} (s^{-1}) at different [H^+] (M)				
	5.0×10^{-2}	7.5×10^{-2}	1.0×10^{-1}	1.25×10^{-1}	1.5×10^{-1}
16	2.43	3.48	4.80	6.29	7.99
25	4.84	6.55	8.99	11.8	15.2
35	8.96	12.1	16.3	20.9	27.7
45	16.9	21.7	29.1	43.7	56.4

^{a}[complex] $= 2.0 \times 10^{-4}$ M and $\mu = 0.15$ ($NaClO_4$).

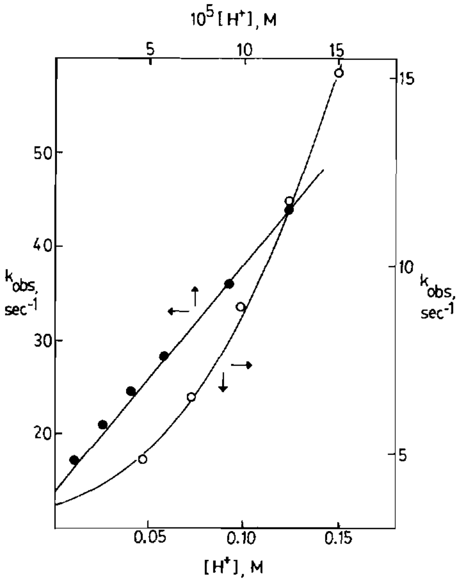


Fig. 2. Plots of k_{obs} *vs.* [H^+] for the acid-catalysed dissociation reactions of $PbEGTA^{2-}$ (●) and $CuEGTA^{2-}$ (○) complexes. (Solid lines are best fit on the basis of regression analysis.)

The rate law which incorporates both the available pathways has two terms and is given as Rate = $\{k_d + k_H[H^+]\}$[complex]. A comparison of k_d and k_H values of $PbEGTA^{2-}$ with a similar value [14] for the Pb(II) complex of cyclohexylenediaminetetraacetic acid (CyDTA) suggests that these rate constants are about 4 to 5 orders of magnitude higher for $PbEGTA^{2-}$ reflecting its lower thermodynamic stability as compared to that of $PbCyDTA^{2-}$. The log *K* values for the reaction $Pb^{2+} + L^{4-} \rightleftharpoons PbL^{2-}$ (where L = EGTA or CyDTA) are 14.5 and 20.2, respectively [13]. A lower stability constant is a result of weaker interaction between the metal ion and ligand, and this shows in the ease of protonation of coordinating group(s) for $PbEGTA^{2-}$. The site of electrophilic attack of the proton is likely to be the amino nitrogen(s) of EGTA as suggested by the equilibrium constants for the protonation of the free ligand [13]. The values in log scale are 9.47 and 8.85 for amino nitrogens; 2.66 and 2.0 for carboxylates. In the concentration range of acid used to study the dissociation of $PbEGTA^{2-}$, carboxylate groups are very unlikely to be protonated.

The buffering anions such as acetate ion are known to catalyse the dissociation of metal complexes either by direct nucleophilic attack on the coordinated metal ion displacing the ligand from the complex, or by forming a new mixed-ligand complex and thus labilising the complex towards ligand loss [15]. To find if the acetate ion in the buffer is playing any role in the dissociation of $PbEGTA^{2-}$, we studied the rate of dissociation of this complex at 25 °C at a constant ionic strength and pH but varying [acetate]. The observed rate constants under these conditions are within experimental error, with a mean value of $(2.64 \pm 0.04) \times 10^1$ s^{-1}. The independence of the dissociation rate on [acetate] is not surprising because the tendency of $PbEGTA^{2-}$ to further complex with the acetate ion is not ap-

TABLE III. Revolved Rate Constants for Dissociation[a] of $\mathrm{PbEGTA^{2-}}$ and $\mathrm{CuEGTA^{2-}}$

Complex	Temperature (°C)	k_d (s^{-1})	k_H ($M^{-1}\ s^{-1}$)	$10^{-2}\,k_{H^2}$ ($M^{-2}\ s^{-1}$)
$\mathrm{PbEGTA^{2-}}$	16	5.37 ± 0.19	(1.44 ± 0.05) X 10^5	
	25	13.8 ± 0.4	(2.44 ± 0.10) X 10^5	
	35	26.6 ± 1.3	(5.09 ± 0.33) X 10^5	
$\mathrm{CuEGTA^{2-}}$ [b]	16	0.90 ± 0.07	22.1 ± 1.5	1.68 ± 0.8
	25	2.84 ± 0.23	18.2 ± 5.0	4.29 ± 0.25
	35	6.40 ± 1.31	8.7 ± 28.4	8.82 ± 1.41
	45	16.16 ± 6.10	−121.0 ± 132.6	26.29 ± 6.56
$\mathrm{CuEGTA^{2-}}$ [c]	16	1.77 ± 0.12		2.88 ± 0.19
	25	3.57 ± 0.10		5.26 ± 0.15
	35	6.72 ± 0.21		9.31 ± 0.32
	45	11.4 ± 1.3		19.5 ± 0.2

[a] From the rate-data presented in Tables I and II. Error limits represent one standard deviation. [b] Fitted to the rate law, Rate = $\{k_d + K_H[H^+] + k_{H^2}[H^+]^2\}$[complex]. [c] Fitted to the rate law, Rate = $\{k_d + k_{H^2}[H^+]^2\}$[complex].

parently significant either due to the fact that Pb(II) is coordinatively saturated or the unfavorable charge on the complex. The possibility of a direct attack of the acetate ion on the metal in $\mathrm{PbEGTA^{2-}}$ is also somewhat restricted because of the wrapping of EGTA around the metal ion which may not leave much room for the acetate ion to attack the metal.

Dissociation Kinetics of CuEGTA^{2-}

The dissociation rates of $\mathrm{CuEGTA^{2-}}$ have been studied in the pH range 0.82–1.30, and three parallel pathways could be present. They are acid-independent or self-dissociation pathways and acid-catalysed pathway(s). The former pathway is similar in both Pb(II) and Cu(II) complexes, but the latter complex shows a different type of dependence on acid concentration. A plot of k_{obs} *versus* $[H^+]$ for $\mathrm{CuEGTA^{2-}}$ is non-linear (Fig. 2) and curves away from abscissa with increase in acid concentration. This is rather typical of a reaction which is more than first-order in $[H^+]$. The overall mechanism for the decomplexation of $\mathrm{CuEGTA^{2-}}$ is proposed in the following reaction scheme

$$\mathrm{CuEGTA^{2-}} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} \{\mathrm{CuEGTA^{2-}}\}^* \underset{\text{fast}}{\overset{2\mathrm{H^+}}{\rightleftharpoons}} \mathrm{Cu^{2+} + H_2EGTA^{2-}} \qquad (1)$$

$$\mathrm{CuEGTA^{2-} + H^+} \xrightarrow{k_H} \mathrm{CuHEGTA^-} \xrightarrow[\text{fast}]{\mathrm{H^+}} \mathrm{Cu^{2+} + H_2EGTA^{2-}} \qquad (2)$$

$$\mathrm{CuEGTA^{2-} + 2H^+} \xrightarrow{k_{H^2}} \mathrm{Cu^{2+} + H_2EGTA^{2-}} \qquad (3)$$

The rate law consistent with the above scheme is Rate = $\{k_d + k_H[H^+] + k_{H^2}[H^+]^2\}$[complex]. The experimental data at several different temperatures can be fitted to the rate law by the method of polynomial regression analysis and the resolved rate constants are listed in Table III. It is interesting to observe that the k_H value decreases as temperature increases and it is even negative at 45 °C. This indicates that the second pathway (eqn. (2)) if present, must not be significant at a higher temperature. On the other hand, if the experimental data are fitted to the rate law, Rate = $\{k_d + k_{H^2}[H^+]^2\}$[complex], the variances of the fit are smaller for high temperature data; the resolved rate constants are listed in Table III. The second-order dependence on [acid] observed for $\mathrm{CuEGTA^{2-}}$ is possibly due to its greater thermodynamic stability as compared to analogous Pb(II) complex and also because of the acid concentration range in which the dissociation of this complex is studied. At higher acid concentrations the carboxylate groups of EGTA can also get protonated in addition to amino nitrogens. Second-order dependence on acid was also observed for some metal carboxylate complexes at relatively high acid concentrations [6].

The water-exchange rate constant for $\mathrm{Cu(H_2O)^{2+}}$, which is very close to the formation rate constant [7] of its complexes, is $\sim 10^8\ s^{-1}$. Knowing the equilibrium and rate constant for the formation of a complex, one can calculate its k_d using the expression $K = k_f/k_d$ if the ligand is lost in one step. The value of k_d obtained for $\mathrm{CuEGTA^{2-}}$ from the above expression is $10^8\ M^{-1}\ s^{-1}/10^{17.5}\ M^{-1} = 10^{-9.5}\ s^{-1}$, which is indistinguishable from zero under our experimental conditions. The experimentally obtained k_d value at 25 °C is 3.57 s^{-1} and is about 10^{10} times faster than the calculated value, indicating that direct dissociation of the complex involves a rate-determining distortion (chelate ring-opening) of the complex to give an intermediate that is scavenged rapidly by hydrogen ion or solvent molecules to yield hydrated Cu(II) ion and free ligand. The identity of the intermediate $\{CuEGTA^{2-}\}^*$ can be established if the equilibrium constant for the following reaction is known:

$$Cu^{2+} + EGTA^{4-} \overset{K'}{\rightleftharpoons} \{CuEGTA^{2-}\}^*$$

It can be calculated indirectly from the values of k_d and k_f for the reaction

$$CuEGTA^{2-} \overset{K''}{\rightleftharpoons} \{CuEGTA^{2-}\}^*$$

which are 3.57 s^{-1} and 10^8 s^{-1} (maximum value), respectively. The equilibrium constant K'' for this reaction is therefore $3.57/{\sim}10^8$ or 3.57×10^{-8}. Given the value of K for the reaction

$$Cu^{2+} + EGTA^{4-} \overset{K}{\rightleftharpoons} CuEGTA^{2-}$$

to be $10^{17.5}$ M^{-1} and the value of K' as 3.57×10^{-8}, it is easy to calculate K' from the relation $K = K'/K''$. The value of K' so calculated is 8.9×10^8 M^{-1} and is very close to the equilibrium constant for the formation of the Cu(II) iminodiacetate (IDA) complex [13], which is 10^{10} M^{-1}. The active intermediate $\{CuEGTA^{2-}\}^*$ in the dissociation of $CuEGTA^{2-}$ contains the metal ion bonded to an amino diacetate moiety, *i.e.* one amino group and two carboxylates groups of EGTA. Margerum and coworkers [16] have strongly argued that an intermediate of this type exists in the exchange reaction of $NiEDTA^{2-}$ with Cu^{2+}. In this exchange reaction they observe Cu^{2+} ion catalysis through the formation of an intermediate CuNiEDTA, in which each metal ion is bonded to one aminodiacetate moiety. The kinetic evidence for the possible existence of such binuclear intermediates in solution has prompted us to investigate the dissociation kinetics of the binuclear copper complex of EGTA, *i.e.* Cu_2EGTA; but our attempts were unsuccessful. The equilibrium constant for the reaction

$$CuEGTA^{2-} + Cu^{2+} \rightleftharpoons Cu_2EGTA$$

is about $10^{4.3}$ M^{-1}. We made this complex *in situ* by using ten fold excess of Cu^{2+} and the complex concentration before the initiation of kinetic runs was 4.0×10^{-4} M. Under such conditions the majority of the complex exists in the binuclear form. Spectroscopic evidence for the existence of the binuclear species comes from the conspicuous disappearance of a shoulder at 291 nm that belongs to $CuEGTA^{2-}$. Attempted rate measurements were made by following the decrease in absorbance of the binuclear complex at 280 nm. A very fast dissociation of Cu_2EGTA to yield $CuEGTA^{2-}$ and Cu^{2+} has been found which is followed by decomplexation of the mononuclear complex. At 0.05 M $[H^+]$ the dissociation of $CuEGTA^{2-}$ was not complete due to the presence of excess of $Cu_{aq}{}^{2+}$, but at higher $[H^+]$ this reaction goes to completion at the same rate as was measured for $CuEGTA^{2-}$ in the absence of any $Cu_{aq}{}^{2+}$. The rapid dissociation of Cu_2EGTA to $CuEGTA^{2-}$ is somewhat predictable. From its equilibrium and formation rate constant the minimum k_d value calculated is $10^{3.7}$ s^{-1} and rate constants of such magnitude cannot be measured on conventional stopped-flow spectrophotometers. Hence it is concluded that within the dead-time of the instrument the conversion of Cu_2EGTA to $CuEGTA^{2-}$ is complete.

Activation Parameters

Enthalpy and entropy of activation for $CuEGTA^{2-}$ and $PbEGTA^{2-}$ complexes have been determined for both pathways, from the Eyring plots, *i.e.* $\log(k/T)$ *versus* $1/T$. The values so obtained are listed in Table IV. A favourable lower value of $\Delta H_d^{\ddagger}$ in combination with an unfavourable negative entropy ($\Delta S_d^{\ddagger}$) for the self-dissociation pathway is indicative of a rate-determining distortion of the complex before it dissociates completely to give free ligand and metal ion [17]. The probable errors associated with $\Delta H_d^{\ddagger}$ and $\Delta S^{\ddagger}$ values for $PbEGTA^{2-}$ are slightly higher as compared to similar parameters for acid-catalysed pathway because the k_d values used to determine $\Delta H_d^{\ddagger}$ and $\Delta S_d^{\ddagger}$ are obtained from the extrapolation of observed rate constants to zero-acid concentration and the uncertainty associated with the intercept is larger compared to the slope of this line.

TABLE IV. Activation Parameters[a] for $PbEGTA^{2-}$ and $CuEGTA^{2-}$ Complexes

Complex	$\Delta H_d^{\ddagger}$ (kJ/mol)	$\Delta S_d^{\ddagger}$ (J/K mol)	$\Delta H_H^{\ddagger}$ (kJ/mol)	$\Delta S_H^{\ddagger}$ (J/K mol)	$\Delta H_{H^2}^{\ddagger}$ (kJ/mol)	$\Delta S_{H^2}^{\ddagger}$ (J/K mol)
$PbEGTA^{2-}$	59.4 ± 7.1	−24.2 ± 23.8	46.4 ± 4.2	15.1 ± 13.8		
$CuEGTA^{2-}$ [b]	46.4 ± 2.9	−78.8 ± 9.2			47.2 ± 13.8	−34.7 ± 11.3

[a] Error limits represent one standard deviation. [b] The data were obtained from the fit to the rate law, Rate = $\{k_d + k_{H^2}[H^+]^2\}$-[complex].

The enthalpy and entropy of activation for the acid-catalysed pathway of both $PbEGTA^{2-}$ and $CuEGTA^{2-}$ are typical of the values observed for an associative mechanism. Moreover, the respective $\Delta H^{\ddagger}_{H}$ and $\Delta H^{\ddagger}_{H^2}$ values for the Pb(II) and Cu(II) complexes of EGTA are in good agreement with similar values reported for first-order [18] and second-order [19] acid catalysis in other complexes.

Independence of Dissociation Rates on [Electrolyte]

The total amount of electrolyte in the reaction mixtures has been reported to alter the rates of dissociation of certain complexes [20, 21]. In our previous studies, we found that cationic complexes dissociate at a slower rate when the concentration of electrolyte is increased [12]. This effect has been explained on the basis of ion-pair formation between the cationic complex and anion in the electrolyte. Rate-enhancement by added electrolyte has also been reported for other complexes [22]. To study the effect of electrolyte on the rates of dissociation of the complexes under study, we measured the observed rate constants for both these complexes in the presence of varying concentrations of $NaClO_4$, keeping the other variables such as temperature and pH constant. No influence of electrolyte on these rate constants could be detected in the range of electrolyte concentration studied. The observed rate constants are within experimental errors and the mean value for $PbEGTA^{2-}$ is $(2.41 \pm 0.07) \times 10^1$ s^{-1}; for $CuEGTA^{2-}$, 8.98 ± 0.07 s^{-1}. It is not certain if the electrolyte has no effect on dissociation rates of these complexes or it has compensation effects on the parallel pathways involved.

Acknowledgements

This material was prepared with the support of U.S. Department of Energy Grant No. DE-FG05-84ER13292; however, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE. One of us (S.S.) is thankful to ACS project SEED for financial support.

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