Reaction between Chromium(III) and EDTA ions: An Overlooked Mechanism of Case Study Reaction of Chemical Kinetics

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SUPPLEMENTARY MATERIAL

An Attempt of Quantification of Constants in Reaction Mechanism – Supplemetary Material

According to the simplified mechanism it will be assumed that Cr(III) ions in the initial reactant solution exist only in the form of $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5(OH)]^{2+}$ ions and that the equilibrium between these two species is determined by acidity constant $K = 1.0 \cdot 10^{-4}$. Further, in the quantitative model constants of formation of ion pairs between chromium(III) ions (hexaaquachromium(III) ion and pentaaquahydroxochromium(III) ion) and EDTA species will not be explicitly taken into account. The consequence of this latter simplification is that the rate of this reaction step will be directly dependent both on the concentration of unreacted Cr(III) ions and concentration of unreacted EDTA species. Further, in order to simplify calculations, acid-base equilibria among intermediates will be ignored.

It will be assumed that in the given pH-range from all possible EDTA species only H_2EDTA^{2-} and $HEDTA^{3-}$ are important; concentration of all other species EDTA species will be taken to be equal to 0. Therefore, in the initial solution only reactive species will be $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_5(OH)]^{2+}$, H_2EDTA^{2-}, and $HEDTA^{3-}$ taken into account. Both chromium species can react with either H_2EDTA^{2-} or $HEDTA^{3-}$ species. These four combinations of reaction between Cr(III) and EDTA ions will be considered as a first (slow and therefore rate-determining) step in overall reaction between Cr(III) and EDTA. This step represents entering of EDTA species into inner sphere of unreacted Cr(III) ion and will be taken to be of the first order regarding to both reactants.

$$[Cr(H_2O)_6]^{3+} + H_2EDTA^{2-} \xrightarrow{k_{Ia}} [Cr(H_2O)_5(H_2EDTA)]^{+} \qquad (1)$$

$$[Cr(H_2O)_6]^{3+} + HEDTA^{3-} \xrightarrow{k_{Ib}} [Cr(H_2O)_5(HEDTA)] \qquad (2)$$

$$[Cr(H_2O)_5(OH)]^{2+} + H_2EDTA^{2-} \xrightarrow{k_{Ic}} [Cr(H_2O)_4(OH)(H_2EDTA)] \qquad (3)$$

$$[Cr(H_2O)_5(OH)]^{2+} + HEDTA^{3-} \xrightarrow{k_{Id}} [Cr(H_2O)_4(OH)(HEDTA)]^{-} \qquad (4)$$

In the literature, it is usually taken that the upper reactions occur with preassociation to ion-pairs. Here a simplified approach that ignores preassociation will be followed. This choice is partially supported with the fact that in our experiment molar concentration of EDTA is lower than 0.1 M and thus the rate of reaction is dependent on EDTA concentration. The other reason for this simplification is to avoid excessive complexity of the used model.

In the second step, which is considerably faster than the first step, intermediates ($[Cr(H_2O)_5(H_2EDTA)]^+$, $[Cr(H_2O)_5(HEDTA)]$, $[Cr(H_2O)_4(OH)(H_2EDTA)]$, and $[Cr(H_2O)_4(OH)(HEDTA)]^-$) formed in the first (slow) step are quickly transformed into the final product of reaction, $[Cr(EDTA)]^-$. It is supposed that all these reactions proceed much faster than the entrance of EDTA ligand into the inner-sphere of Cr(III) ions. Since these reactions are not the bottleneck of the overall reaction and because there are no data available about the values of these rate constants, we may then ascribed the same rate constant, k_{II}, to all these reactions:

$$[Cr(H_2O)_5(H_2EDTA)]^+ \xrightarrow{k_{\mathrm{II}}} [Cr(EDTA)]^- \quad (5)$$

$$[Cr(H_2O)_5(HEDTA)] \xrightarrow{k_{\mathrm{II}}} [Cr(EDTA)]^- \quad (6)$$

$$[Cr(H_2O)_4(OH)(H_2EDTA)] \xrightarrow{k_{\mathrm{II}}} [Cr(EDTA)]^- \quad (7)$$

$$[Cr(H_2O)_4(OH)(HEDTA)]^- \xrightarrow{k_{\mathrm{II}}} [Cr(EDTA)]^- \quad (8)$$

The concentration ratio between more reactive $[Cr(H_2O)_5(OH)]^{2+}$ species and more stable $[Cr(H_2O)_6]^{3+}$ species that are entering in the first step of reaction, is determined by the acidity constant K, concentration of H^+ ions, and individual activity coefficients γ of all species involved in the equilibrium:

$$[Cr(H_2O)_6]^{3+} \xleftrightarrow{K} [Cr(H_2O)_5(OH)]^{2+} + H^+ \quad (10)$$

$$K = \frac{c_{[\mathrm{Cr(H_2O)_5(OH)}]^{2+}} \gamma_{[\mathrm{Cr(H_2O)_5(OH)}]^{2+}} c_{\mathrm{H^+}} \gamma_{\mathrm{H^+}}}{c_{[\mathrm{Cr(H_2O)_6}]^{3+}} \gamma_{[\mathrm{Cr(H_2O)_6}]^{3+}}} \quad (11)$$

The overall rate of the reaction is given by the rate of formation of the product $[Cr(EDTA)]^-$:

$$v = \frac{dc_{[Cr(EDTA)]^-}}{dt} = k_{\mathrm{II}} c_{\mathrm{I}} \quad (12)$$

where c_{I} denotes sum of concentrations of all intermediates (i.e. $[Cr(H_2O)_5(H_2EDTA)]^+$, $[Cr(H_2O)_5(HEDTA)]$, $[Cr(H_2O)_4(OH)(H_2EDTA)]$, and $[Cr(H_2O)_4(OH)(HEDTA)]^-$):

$$c_{\mathrm{I}} = c_{[\mathrm{Cr(H_2O)_5(H_2EDTA)}]^+} + c_{[\mathrm{Cr(H_2O)_5(HEDTA)}]} + c_{[\mathrm{Cr(H_2O)_4(OH)(H_2EDTA)}]} + c_{[\mathrm{Cr(H_2O)_4(OH)(HEDTA)}]^-} \quad (13)$$

The overall concentration of intermediates then changes with time according to the expression

$$\frac{dc_{\mathrm{I}}}{dt} = k_{\mathrm{Ia}} c_{[\mathrm{Cr(H_2O)_6}]^{3+}} c_{\mathrm{H_2EDTA^{2-}}} + k_{\mathrm{Ib}} c_{[\mathrm{Cr(H_2O)_6}]^{3+}} c_{\mathrm{HEDTA^{3-}}} + k_{\mathrm{Ic}} c_{[\mathrm{Cr(H_2O)_5(OH)}]^{2+}} c_{\mathrm{H_2EDTA^{2-}}} + k_{\mathrm{Id}} c_{[\mathrm{Cr(H_2O)_5(OH)}]^{2+}} c_{\mathrm{HEDTA^{3-}}} - k_{\mathrm{II}} c_{\mathrm{I}}$$

(14)

If we assume additivity of volumes then the sum of concentrations of all chromium species has to be equal to the initial concentration of chromium(III) ions, c_0:

$$c_0 = c_{[\mathrm{Cr(H_2O)_6}]^{3+}} + c_{[\mathrm{Cr(H_2O)_5(OH)}]^{2+}} + c_{\mathrm{I}} + c_{[\mathrm{Cr(EDTA)}]^{-}} \qquad (15)$$

Ionic equilibria among EDTA species will be simplified to consider only concentrations of species H_2EDTA^{2-} and $HEDTA^{3-}$ (sum of concentration of these two species will be equal to the total concentration of unreacted EDTA); concentrations of other EDTA species will be taken to be equal to 0. This simplification is reasonable taking that the concentrations of H_4EDTA, H_3EDTA^-, and $EDTA^{4-}$ species are very low in the given pH-range. The ratio between concentration of $HEDTA^{3-}$ and H_2EDTA^{2-} is determined by the dissociation constant $k_{\mathrm{EDTA}} = 7.41 \cdot 10^{-7}$, concentration of H^+ ions, and individual activity coefficients γ of all species involved in the equilibrium:

$$k_{\mathrm{EDTA}} = \frac{c_{\mathrm{HEDTA^{3-}}} \gamma_{\mathrm{HEDTA^{3-}}} c_{\mathrm{H^+}} \gamma_{\mathrm{H^+}}}{c_{\mathrm{H_2EDTA^{2-}}} \gamma_{\mathrm{H_2EDTA^{2-}}}} \qquad (16)$$

We will further assume that the activity coefficients are dependent only on absolute electric charge of the given species and the ionic strength of the solution. Due to high concentration of $NaNO_3$ (1 M solution) ionic strength will be taken as constant during course of the reaction.

$$\gamma_3 = \gamma_{[\mathrm{Cr(H_2O)_6}]^{3+}} = \gamma_{\mathrm{HEDTA^{3-}}}$$

$$\gamma_2 = \gamma_{[\mathrm{Cr(H_2O)_5(OH)}]^{2+}} = \gamma_{\mathrm{H_2EDTA^{2-}}}$$

$$\gamma_1 = \gamma_{\mathrm{H^+}}$$

Because Debye-Hückel equation for calculation of activity coefficients is of questionable validity at such high ionic strength as it is in solution containing 1 M $NaNO_3$, arbitrary estimated values will be ascribed to activity coefficients γ_1, γ_2, and γ_3: $\gamma_1 = 0.7$; $\gamma_2 = 0.3$; $\gamma_3 = 0.2$.

During numerical solving of equations (1) – (16) experimentally determined pH-values will be used. Namely, in the given system EDTA has only limited buffer capacity and consequently, pH value can be notably changed during course of the reaction. Values of constants that can be determined rather reliably (K, K_{EDTA}) will be taken from literature data while the values of missing rate constants (k_{Ia}, k_{Ib}, k_{Ic}, and k_{Id}) will be initially estimated from values, found for similar systems, and then adjusted to improve concordance of model calculations with the experimental data. In order to avoid excessive number of freely adjustable parameters, two pairs of constants (k_{Ia} and k_{Ic}; k_{Ib} and k_{Id}) will be tied together by the same constant. This constant will be occasionally adjusted during fitting procedure in order to achieve as good as possible concordance of from the model-calculated concentration of the product with the one determined experimentally. According to greater lability of $[Cr(H_2O)_5(OH)]^{2+}$ ion in comparison to lability of $[Cr(H_2O)_6]^{3+}$ it will be assumed, that the values of rate constants k_{Ic} and k_{Id} are greater than the values of constants k_{Ia} and k_{Ib}:

$k_{Ic} = 1000 \cdot k_{Ia}$ and

$k_{Id} = 1000 \cdot k_{Ib}$

Diagram of measured concentration of the final product, $[CrEDTA)]^-$, and its concentration as calculated from the model are represented in Figures 5, 6, and 7 as a function of time for different values of initial pH values. Calculated values were obtained with values $k_{Ia} = 9.75 \cdot 10^{-5}$ dm^3 mol^{-1} min^{-1}, $k_{Ib} = 5.00 \cdot 10^{-3}$ dm^3 mol^{-1} min^{-1}, $k_{Ic} = 9.75 \cdot 10^{-2}$ dm^3 mol^{-1} min^{-1}, $k_{Id} = 5.0$ dm^3 mol^{-1} min^{-1}, and $k_{II} = 3.3 \cdot 10^{-2}$ min^{-1}. Constants k_{Ia}, k_{Ib}, and k_{II} were adjusted manually without invoking computer-driven optimization algorithm. The ultimate adjusting of parameters, representing unknown rates of partial reactions, was omitted. The first reason is that such an adjustment would be most efficiently done with the use of appropriate computer program and that such a program should be written. It would be meaningful to invest this effort when more complex reaction would be involved and therefore more than just very approximate values for constants would be expected to obtain from such model analysis. The second reason is that three independent adjustable parameters are used in the calculations what is close to the upper limit for the analysis of the presented data. In such a case greater number of experiments should be included in the model analysis, i.e. beside pH-values also concentrations of Cr^{3+} and EDTA ions should be varied. Some of the mentioned experiments were done but the reaction rates were sometimes so low that not all these data were suitable for model analysis. The third reason is that also the rate of the second step (formation of hexadentate complex from the monodentate one) is probably pH-dependent reaction step but due to its rapidity this step is difficult to follow. It is interesting that there are no literature data about the second step of the reaction between Cr(III) ions and EDTA; imposing pH-dependence to the rate of this step would be then pure speculation.

In spite of only partially achieved adjustment of model calculations to experimental data it is recognizable that the values of constants k_{Ia}, k_{Ib}, k_{Ic}, and k_{Id} have reasonable figures. When values of k_{Ia} and k_{Ic} are compared with the adjusted (for the concentration of bulk water) rate constants for water exchange in $[\mathrm{Cr(H_2O)_6}]^{3+}$ and $[\mathrm{Cr(H_2O)_5(OH)}]^{2+}$ ions one notices that they (i.e. k_{Ia} and k_{Ic}) are two order of magnitude greater what is a reasonable value when compared to rate constants for comparable ligands.

At the same time, constant k_{Ib} is greater than k_{Ia} (and, respectively, k_{Id} greater than k_{Ic}) what can be regarded as a consequence of greater association constant for association of chromium(III) ions with HEDTA^{3-} species than with $\mathrm{H_2EDTA}^{2-}$ (electrostatic attraction between 3+ and 3- ions is greater than between 3+ and 2- ions). The second explanation would be that HEDTA^{3-} species is more successful in replacing water molecule from the chromium(III) aqua ion than $\mathrm{H_2EDTA}^{2-}$ species. Explanation that is even more probable is, that greater value of k_{Ib} than k_{Ia} is a consequence of both reasons.