

Crystal Field Activation Energy for Ligand Substitution Reactions

The premise:

Ligand exchange rates cover many orders of magnitude. Our task is to explain why this is true using a simple theory. Unfortunately, there are no “intermediate” theories that explain the concepts of *inert* and *labile*, so to really get a good answer would require carrying out high level QM calculations on your system of interest. Instead, let’s see if we can get a reasonable predictive theory using simple crystal/ligand field arguments. The basis of our work will be the concept of Crystal Field Activation Energy (CFAE); the difference in activation energy for the ligand exchange process that is caused by changes in Crystal Field.

Data:

Here is some data collected from several sources that gives the electronic configuration and ligand exchange rate for several classes of transition metal complexes. When the ligand exchange rate is on the order of 10^8 s^{-1} or faster, this approaches the fastest possible rate; a diffusion limited rate can be calculated to be $10^9 - 10^{11} \text{ s}^{-1}$. This rate is seen in alkali metals, alkaline earths and some divalent transition metals. Labile metal complexes have rate constants ranging from $10^4 - 10^8 \text{ s}^{-1}$. While indistinguishable in a practical sense, the rates can be measured. Complexes on the high rate end include divalent transition metals, lanthanides, while slower rate complexes are trivalent transition metals. Inert metal complexes have rates ranging from $10^{-1} - 10^{-8} \text{ s}^{-1}$. These complexes include the “classic” inert ions Cr^{3+} and Co^{3+} .

Divalent $[\text{M}(\text{H}_2\text{O})_6]^{n+}$ complexes (high spin)^{1,2}

Cation	L exchange rate (s^{-1})	e ⁻ config
V(II)	$8.7 \cdot 10^1$	t_{2g}^3
Cr(II)	$1.2 \cdot 10^8$	$t_{2g}^3 e_g^1$
Mn(II)	$2.1 \cdot 10^7$	$t_{2g}^3 e_g^2$
Fe(II)	$4.4 \cdot 10^6$	$t_{2g}^4 e_g^2$
Co(II)	$3.2 \cdot 10^6$	$t_{2g}^5 e_g^2$
Ni(II)	$3.2 \cdot 10^4$	$t_{2g}^6 e_g^2$
Ti(III)	$1.8 \cdot 10^5$	t_{2g}^1
V(III)	$5 \cdot 10^2$	t_{2g}^2
Cr(III)	$2.4 \cdot 10^{-6}$	t_{2g}^3
Fe(III)	$1.6 \cdot 10^2$	$t_{2g}^3 e_g^2$
Co(III)[†]	$5.7 \cdot 10^{-6}$	t_{2g}^6

[†]for low spin $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$

2nd and 3rd row $[\text{M}(\text{H}_2\text{O})_6]^{n+}$ complexes^{1,2}

Cation	L exchange rate (s^{-1})	e ⁻ config
Ru(II)	$1.8 \cdot 10^{-2}$	t_{2g}^6
Ru(III)	$3.5 \cdot 10^{-6}$	t_{2g}^5
Rh(III)	$2.2 \cdot 10^{-9}$	t_{2g}^6
Ir(III)	$1.1 \cdot 10^{-10}$	t_{2g}^6

Low-spin metal cyano complexes³

Anion	CN ⁻ exchange rate (s^{-1})	e ⁻ config
$[\text{V}(\text{CN})_6]^{-4}$	$>1 \cdot 10^{-2}$	t_{2g}^3
$[\text{Cr}(\text{CN})_6]^{-4}$	$>1 \cdot 10^{-2}$	t_{2g}^4
$[\text{Cr}(\text{CN})_6]^{-3}$	$3 \cdot 10^{-7}$	t_{2g}^3
$[\text{Mn}(\text{CN})_6]^{-4}$	$>1 \cdot 10^{-2}$	t_{2g}^5
$[\text{Mn}(\text{CN})_6]^{-3}$	$2 \cdot 10^{-4}$	t_{2g}^4
$[\text{Fe}(\text{CN})_6]^{-4}$	$<1 \cdot 10^{-6}$	t_{2g}^6
$[\text{Fe}(\text{CN})_6]^{-3}$	$<1 \cdot 10^{-6}$	t_{2g}^5
$[\text{Co}(\text{CN})_6]^{-3}$	$<1 \cdot 10^{-6}$	t_{2g}^6

Notice some facts:

Water exchange rates for divalent 3rd row transition metals follow the following order, but it is hard to find a trend: $V^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+} < Cu^{2+}$. V^{2+} is six times slower than V^{3+} .

The water exchange rate for Co^{3+} cannot be measured because this ion oxidizes water, but complexes of Co^{3+} (such as $[Co(en)_3]^{3+}$ or $[Co(NH_3)_6]^{3+}$) are inert while their corresponding Co^{2+} counterparts are labile.⁴

Procedure:

The first step in determining the CFAE is to determine the crystal field stabilization energy for the octahedral complex and the corresponding square pyramidal complex. For the purposes of this exercise we are assuming that the mechanism is dissociative. Tabulated orbital energies as a function of geometry are readily available in most textbooks; for consistency in calculations, values are repeated here in units of Δ_o . When considering changes in geometry, do not change the spin state of the complex.

orbital	O _h	Sq Pyr
d _{xz}	-0.4	-0.457
d _{yz}	-0.4	-0.457
d _{xy}	-0.4	-0.086
d _{z2}	0.6	0.086
d _{x2-y2}	0.6	0.914

1) calculate the CFSE for both O_h and square pyramidal for the following ions (**bolded** in the tables on the previous page) in units of Δ_o :

a) Co(II)

b) Co(III) (low spin)

c) Cr(III)

d) Mn(III)

The $\Delta CFSE$ is the change in crystal field stabilization energy upon undergoing a geometry change. For the purposes of ligand substitution, the geometry change is accompanied by the loss of a ligand.

2) Calculate the $\Delta CFSE$ (Δ_o Sq Pyr - Δ_o O_h) for the geometry change for the following ions in units of Δ_o , consider both water and cyano ligand exchange where possible:

a) Co(II)

b) Co(III) (low spin)

c) Cr(III)

d) Mn(III) (low spin)

3) rank order the four ions in terms of relative $\Delta CFSE$ from most positive to most negative. Does this order relate to the rate of ligand exchange in the above tables?

The $\Delta CFSE$ is just one factor in the rate of a reaction. For ligand dissociation reactions, a much larger term is the *bond breaking* that must occur to reach the intermediate geometry. Average metal ligand bond strengths can be measured or calculated using a Born-Haber cycle. A typical M-NH₃ bond strength for a first row divalent transition metal ion is 60-70 kcal/mol.⁵ The variability in these numbers is large but it is not unreasonable to assume that a M-OH₂ bond strength is similar. Bonus points to a student who can find a good, referenced value for the bond strength of a transition element and water.

The rate constant k of a chemical reaction is proportional to its activation energy by the Eyring equation:

$$k = \left(\frac{k_B T}{h} \right) e^{(-\Delta G^\ddagger/RT)}$$

Calculating a rate with this equation would require knowing the concentrations of the complexes and ligands, which we can assume to be equal across two experiments, so comparing the relative rate constants is the same as comparing the relative rates. The activation energy would be (at a minimum) approximately that of the M-L bond, or 60-70 kcal/mol *plus* the small amount of additional energy for the $\Delta CFSE$ upon moving from the octahedral geometry to the square pyramidal geometry. Calculating the *relative* rate between two metal complexes can be done by dividing terms, cancelling the constants:

$$\frac{k_1}{k_2} = \frac{e^{-\Delta G_1^\ddagger/RT}}{e^{-\Delta G_2^\ddagger/RT}} = e^{-\Delta\Delta G^\ddagger/RT}$$

The $\Delta\Delta G^\ddagger$ term can be approximated as the $\Delta\Delta CFSE$ for the ligand substitution reaction. When you calculated the $\Delta CFSE$, you used units of Δ_o . To convert Δ_o to a better unit for thermodynamics, recall that Δ_o is on the order of 15,000-20,000 cm⁻¹ which corresponds to about 45-55 kcal/mol (approximately that of the M-L bond strength). $R = 1.987$ cal/mol·K and $T = 298$ K. When doing this calculation, think about what it means if you use the positive or negative $\Delta CFSE$ value.

4) Using the $\Delta CFSE$ terms you calculated above, calculate the *relative rates* of ligand substitution for:

a) Co(II) and Co(III) (low spin), water exchange

b) Cr(III) and Mn(III) (low spin), cyanide exchange

c) do the relative rates you calculated here match the relative rates tabulated above?

5) additional practice: verify the relative rates of V^{2+} and V^{3+} . Is the rate order predicted correctly? Is the relative rate ratio predicted correctly?

References

- 1) Ligand substitution rates for high spin metal aquo complexes from Lothar Helm, André E. Merbach "Inorganic and Bioinorganic Solvent Exchange Mechanisms" Chemical Reviews 2005, volume 105, 1923-1959. doi:10.1021/cr030726o.
- 2) Most of these data are also reported in "Inorganic and Organometallic Reaction Mechanisms," 2nd ed., by J. D. Atwood, Wiley-VCH, New York, 1997. Where these values are different from those reported in Atwood, the newer values are listed.
- 3) Ligand substitution rates for 1s metal cyano complexes from "Ions in Solution: Basic Principles of Chemical Interactions," 2nd ed., by J. Burgess, Horwood Publishing, Chichester, West Sussex England, p107.
- 4) the rate law for ammonia exchange in aqueous solutions of Co(II) in varying concentrations of ammonia in water is $3 \cdot 10^7 \text{ sec}^{-1}$. Robert Murray, Stephen F. Lincoln, Hans H. Glaeser, Harold W. Dodgen, and John P. Hunt, *Inorganic Chemistry* **1969** 8 (3), 554-555, DOI: 10.1021/ic50073a028. The rate of water exchange on $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ is $5.7 \cdot 10^{-6}$ (ref 2)
- 5) F. A. Cotton, "Bond Energies in Transition Metal Complexes," *Acta Chem. Scand.* **1956**, 10, 1520-1526.