

9.1.4.2: Associative Mechanisms

Associative mechanisms tend to be less common for octahedral complexes as a result of steric hindrance of the metal ion by six ligands. However, reactions of octahedral complexes with associative character are more likely if the ligands have low steric bulk and/or the central metal ion is larger with longer bonds (as in the case of $4d$ and $5d$ metal ions). Reactions of octahedrons have also been observed in cases of low d -electron count or low electron density around the central ion, presumably making nucleophilic reaction more favorable. If an octahedral complex is determined to have associative character, in most cases it is associatively-active interchange (I_a).

The evidence that supports arguments for associative mechanisms is somewhat the opposite as that which would support dissociative character. One typical piece of evidence that supports an associative pathway is **a large effect of the incoming ligand on the reaction rate constant**. For example, in the reaction of hexaaquo chromium (III) ion ($[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$) with various incoming ligands (shown below), rate constants vary by several orders of magnitude. This data is evidence of an associative mechanism (I_a). In contrast, the reaction of pentaammineaquo chromium (III) ion ($[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$) occurs by an associative mechanism (data shown in [Section 12.4.1](#)). The difference in reaction mechanisms for different chromium (III) complexes can be justified by the different electron densities around their metal ion center. The ammine ligand is a stronger sigma donor and thus the metal center is more electron rich in the case of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$. Nucleophilic reaction by an incoming ligand is thus more likely in the case of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, which has a more electrophilic center.

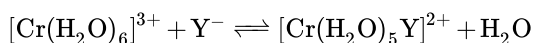


Table 9.1.4.2.1 : Rate Constants for Exchange of Aquo Ligand of hexaaquo chromium(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's *Inorganic Chemistry*, 5th edition, pg 449.

Entering Ligand, Y^-	Rate Constant, k_1 ($10^{-4} \text{ M}^{-1} \text{ s}^{-1}$)
NCS^-	180
NO_3^-	73
Cl^-	2.9
Br^-	0.9
I^-	0.08

Another piece of evidence that can support associative mechanisms is the temperature-dependence of the rate law, which in turn can yield the entropy of activation (represented as ΔS^\ddagger or ΔS_{act}). When an incoming ligand associates with a metal complex and two molecules become one, there would be a negative change in the entropy (entropy decreases). A negative value for the entropy of activation indicates an associative pathway. An example of this is in the substitution of the aquo ligand in $[\text{Ru}(\text{EDTA})(\text{H}_2\text{O})]^-$, which has a negative value of ΔS^\ddagger , indicating an I_a mechanism.

This page titled [9.1.4.2: Associative Mechanisms](#) is shared under a [not declared](#) license and was authored, remixed, and/or curated by [Kathryn Haas](#).