

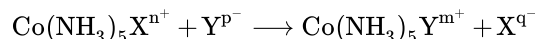
5.16: The Mechanism of the Base Hydrolysis of $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$

This chapter focuses on the relationship between rate laws and reaction mechanisms. We have noted that the rate law is rarely sufficient to establish the mechanism of a particular reaction. The base hydrolysis of cobalt pentammine complexes is a reaction for which numerous lines of evidence converge to establish the mechanism. To illustrate the range of data that can be useful in the determination of reaction mechanisms, we summarize this evidence here.

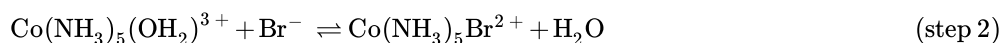
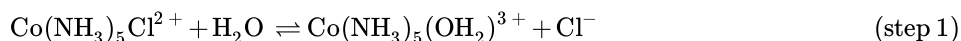
Cobalt(III) complexes usually undergo substitution reactions at readily measurable rates. Cobalt pentammine complexes, $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$, have been studied extensively.

Mechanism 1

In acidic aqueous solutions, the reaction



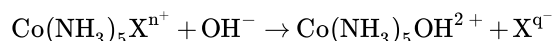
(X^{q-} , Y^{p-} = Cl^- , Br^- , NO_2^- , SCN^- , CH_3CO_2^- , etc.) usually proceeds exclusively through the aquo complex, $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$. The first step in the reaction is the breaking of a Co–X bond and the formation of a Co–OH₂ bond (step 1). Subsequently, a Y^{p-} moiety can replace the aquo group (step 2). For example:



In aqueous solution, water is always present at a much higher concentration than the various possible entering groups Y^{p-} , so it is reasonable that it should be favored in the competition to form the new bond to Co(III). Nevertheless, we expect the strength of the Co–Y bond to be an indicator of the nucleophilicity of Y^{p-} in these substitution reactions. The fact that the aquo complex is the predominant reaction product strongly suggests that the energetics of the reaction are dominated by the breaking of the Co–X bond; formation of the new bond to the incoming ligand apparently has little effect. Whether the old Co–X bond has been completely broken (so that $\text{Co}(\text{NH}_3)_5^{3+}$ is a true intermediate) before the new Co–OH₂ bond has begun to form remains an issue on which it is possible to disagree.

Mechanism 2

There is a conspicuous exception to the description given above. When the entering group, Y^{p-} , is the hydroxide ion, the reaction is



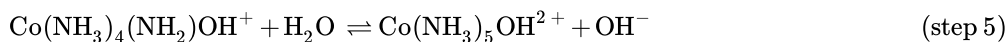
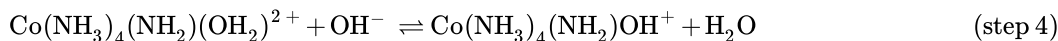
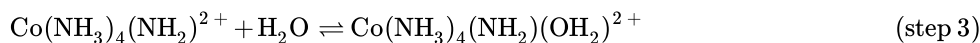
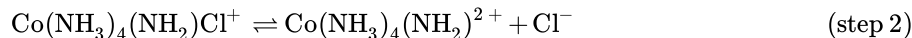
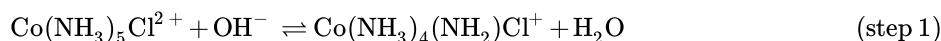
This is called the **base-hydrolysis reaction**. It is faster than the formation of the aquo complex in acidic solutions, and the rate is law found to be

$$\frac{d[\text{Co}(\text{NH}_3)_5\text{OH}^{2+}]}{dt} = k [\text{Co}(\text{NH}_3)_5\text{X}^{n+}] [\text{OH}^-]$$

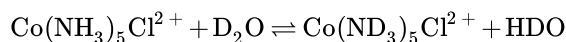
This rate law is consistent with S_N2 nucleophilic attack by the hydroxide ion at the cobalt center, so that Co–OH bond formation occurs simultaneously with breaking of the Co–X bond. However, this interpretation means that the hydroxide ion is a uniquely effective nucleophile toward cobalt(III). Nucleophilic displacements have been investigated on many other electrophiles. In general, hydroxide is not a particularly effective nucleophile toward other electrophilic centers. So, assignment of an S_N2 mechanism to this reaction is reasonable only if we can explain why hydroxide is uniquely reactive in this case and not in others.

Mechanism 3

An alternative mechanism, usually labeled the S_N1CB (Substitution, Nucleophilic, first-order in the Conjugate Base mechanism), is also consistent with the second-order rate law. In this mechanism, hydroxide removes a proton from one of the ammine ligands, to give a six-coordinate intermediate, containing an amido (NH_2^-) ligand (step 1). This intermediate loses the leaving group X^{q-} in the rate determining step to form a five-coordinate intermediate, $\text{Co}(\text{NH}_3)_4\text{NH}^{2+}$ (step 2). This intermediate picks up a water molecule to give the aquo complex (step 3). In a series of proton transfers to (step 4) and from (step 5) the aqueous solvent, the aquo complex rearranges to the final product. With Cl^- as the leaving group, the S_N1CB mechanism is



The evidence in favor of the $\text{S}_{\text{N}}1\text{CB}$ mechanism is persuasive. It requires that the ammine protons be acidic, so that they can undergo the acid–base reaction in the first step. That this reaction occurs is demonstrated by proton-exchange experiments. In basic D_2O , the ammine protons undergo H–D exchange according to



The ammine protons are also necessary; base hydrolysis does not occur for similar compounds, like $\text{Co}(2,2'\text{-bipyridine})_2(\text{O}_2\text{CCH}_3)_2^+$, in which there are no protons on the nitrogen atoms that are bound to cobalt (*i.e.*, there are no H–N–Co moieties).

The evidence that $\text{Co}(\text{NH}_3)_4(\text{NH}_2)^{2+}$ is an intermediate is also persuasive. When the base hydrolysis reaction is carried out in the presence of other possible entering groups, Y^{p-} , the *rate* at which $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ is consumed is unchanged, but the product is a mixture of $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Y}^{n+}$. If this experiment is done with a variety of leaving groups, X^{q-} , the proportions of $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Y}^{n+}$ are constant—independent of which leaving group the reactant molecule contains. These observations are consistent with the hypothesis that all reactants, $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$, give the same intermediate, $\text{Co}(\text{NH}_3)_4(\text{NH}_2)^{2+}$. The product distribution is always the same, because it is always the same species undergoing the product-forming reaction.

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