

### ► 11.3.5 *Base Hydrolysis*

Replacement of a ligand by  $\text{OH}^-$  is called **base hydrolysis** [Equation (11.1),  $\text{Y} = \text{OH}^-$ ]. In  $\text{Co}^{\text{III}}$  complexes containing amine ligands, the rate of base hydrolysis is very much faster than acid hydrolysis (aquation). Compare the second-order rate constants for base hydrolysis in Table 11.16 with aquation rate constants (Tables 11.4 and 11.6). Base hydrolysis is ordinarily second-order and never seems to reach the mixed-order behavior (rate saturation) of the rate laws for the **D** and **I<sub>d</sub>** mechanisms (Section 11.3.3). Base hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  obeys the rate expression

<sup>18</sup> One seemingly simple piece of evidence of a **D** mechanism would be the observation of the mass-law retardation by **X** predicted in Equation (11.6). However, it has been shown that outer-sphere complexation by **X** released in the reaction leads to a rate law of the same form. See J. A. Ewen and D. J. Darensbourg, *J. Am. Chem. Soc.* **1976**, *98*, 4317.

Table 11.16 Rate constants for base hydrolysis of some octahedral complexes<sup>a, b</sup>

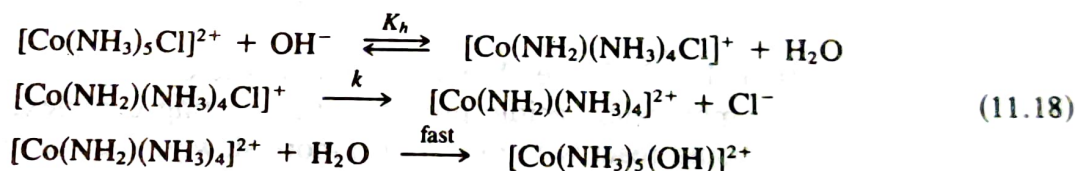
Complex	$k$ ( $M^{-1} s^{-1}$ ) (25°C)	Complex	$k$ ( $M^{-1} s^{-1}$ ) (0°C)
$[Co(NH_3)_5OP(OMe)_3]^{3+}$	79	<i>cis</i> - $[Co(OH)(en)_2Cl]^+$	0.37
$[Co(NH_3)_5NO_3]^{2+}$	5.5	<i>trans</i> - $[Co(OH)(en)_2Cl]^+$	$1.7 \times 10^{-3}$
$[Co(NH_3)_5I]^{2+}$	3.2	<i>cis</i> - $[Co(en)_2Cl_2]^+$	15.1
$[Co(NH_3)_5Cl]^{2+}$	0.23	<i>trans</i> - $[Co(en)_2Cl_2]^+$	85
$[Co(NH_3)_5SO_4]^+$	$4.9 \times 10^{-2}$	<i>cis</i> - $[Co(en)_2(NH_3)Cl]^{2+}$	0.50
$[Co(NH_3)_5F]^{2+}$	$1.3 \times 10^{-2}$	<i>trans</i> - $[Co(en)_2(NH_3)Cl]^{2+}$	1.25
$[Co(NH_3)_5(NCS)]^{2+}$	$5.0 \times 10^{-4}$	<i>cis</i> - $[Co(CN)(en)_2Cl]^+$	$8.9 \times 10^{-3}$
$[Co(NH_3)_5N_3]^{2+}$	$3.0 \times 10^{-4}$	<i>trans</i> - $[Co(en)_2(CN)Cl]^+$	0.13

<sup>a</sup>Leaving ligand written last.

<sup>b</sup>From the work of Lalor, Chan, Bailar, Taube, Basolo, Pearson, Wallace, Kane-Maguire, and others.

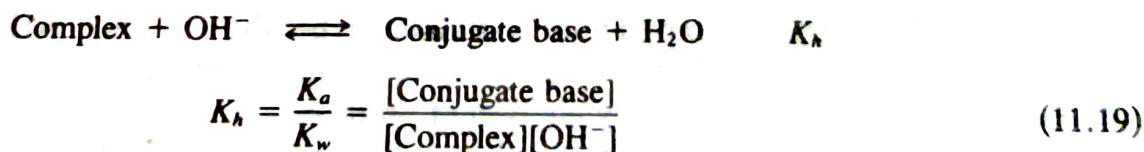
$$\text{rate} = k[Co(NH_3)_5Cl^{2+}][OH^-] \quad (11.17)$$

up to  $[OH^-] = 1.0 M$ . These facts point to a special mechanism for base hydrolysis. In fact, it was argued for some time that base hydrolysis provided an example of an **A** reaction involving rate-determining attack by  $OH^-$ . However, it would be extremely surprising if  $OH^-$  were the *only* nucleophile in aqueous solution capable of attack. Currently, the mechanism first proposed by Garrick in 1937 is considered to operate:



The first step involves the proton removal by  $OH^-$  in a rapid acid–base equilibrium, giving a complex ion of lower charge that loses  $Cl^-$  more rapidly than the starting complex. The last step is relatively fast, so the second step is rate-determining. This is referred to as a **D–CB** mechanism, indicating that it involves a **D** reaction of the conjugate base (**CB**) of the starting complex<sup>19</sup> (Figure 11.6).

The rate law [Equation (11.17)] is easily shown to be consistent with the **D–CB** mechanism if the first step of Equation (11.18) is a rapidly established equilibrium. The rate would be first-order in conjugate base  $[CoCl(NH_2)(NH_3)_4]^+$ , but the concentration of conjugate base can be related to the concentrations of the initial complex and  $OH^-$ . Consider the hydrolysis reaction



$$[\text{Conjugate base}] = \frac{K_a[\text{Complex}][OH^-]}{K_w} \quad (11.20)$$

<sup>19</sup>In the older literature, this is referred to as the  $S_N1CB$  mechanism.

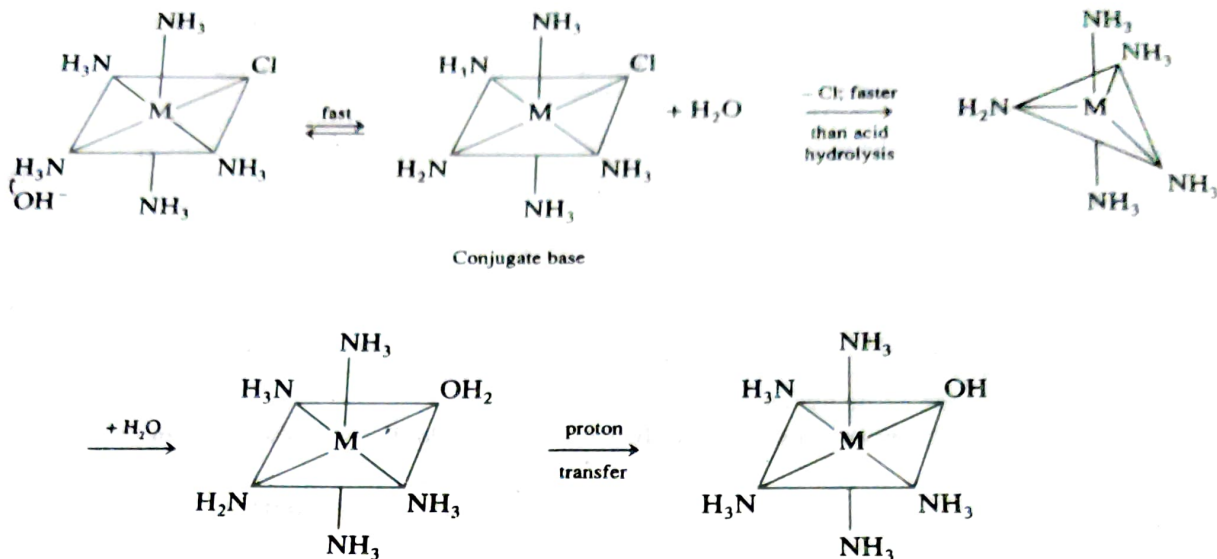


Figure 11.6 The D-CB mechanism.

Because

$$\text{rate} = k'[\text{Conjugate base}] = k' \frac{K_a}{K_w} [\text{Complex}][\text{OH}^-] \quad (11.21)$$

Equation (11.17) is the observed rate law where  $k = k' K_a / K_w$ . The D-CB mechanism requires a moderately acidic proton in the starting complex. A complex without an acidic proton should react with  $\text{OH}^-$  much more slowly, and the rate would be expected to be independent of  $[\text{OH}^-]$ . This, in fact, is observed for the base hydrolysis of  $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$  and *trans*- $[\text{Co}(\text{py})_4\text{Cl}_2]^+$ . However,  $[\text{Pt}(\text{CN})_4\text{Br}_2]^{2-}$ , *cis*- $[\text{CoL}_2\text{Cl}_2]^+$  ( $L = \text{bipy}$ , phen), and *cis*- $[\text{CrL}_2\text{Cl}_2]^+$  ( $L = \text{bipy}$ , phen)<sup>20</sup> all undergo base hydrolysis in spite of a lack of acidic protons for reasons that are not well understood.

The important features of the Garrick mechanism [Equation (11.18)] have been well documented in the literature.<sup>21</sup> The conjugate base is believed to be about  $10^6$  more reactive to substitution than the parent. A true five-coordinate intermediate is produced having trigonal-bipyramidal geometry (unless the ligands are too rigid to rearrange). The existence of the intermediate is inferred by several lines of evidence.

### Effects of Nonleaving Ligands

The trigonal bipyramid is stabilized by the  $\pi$ -donor  $\text{NH}_2^-$ . (See Figure 11.4, where  $L = \text{NH}_2^-$ .) On rearrangement to a trigonal bipyramid, ligands both *cis* and *trans* to the leaving group occupy equivalent positions. Hence, the reactivities of *trans*- $[\text{CoL}(\text{en})_2\text{Cl}]^+$  reflect  $\pi$ -donor abilities of L. The low reactivity for  $X = \text{CN}^-$  is related to its  $\pi$ -acceptor

<sup>20</sup>J. Josephson and C. E. Schaeffer, *J. Chem. Soc., Chem. Commun.* 1970, 61.

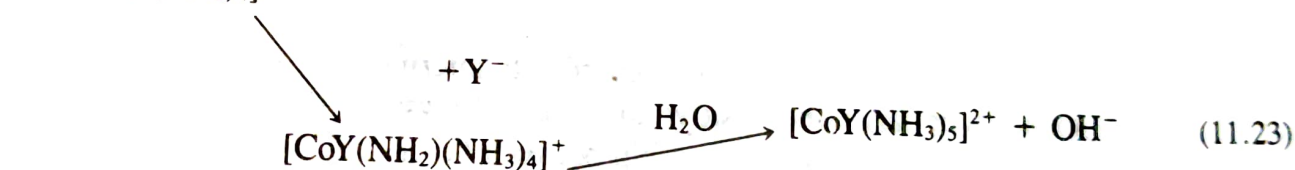
<sup>21</sup>An excellent overall review is provided by M. L. Tobe, *Acc. Chem. Res.* 1970, 3, 377.

properties. Although a good  $\pi$ -donor *cis* to the leaving ligand can donate electrons without the necessity for rearrangement to a trigonal bipyramid, it seems likely that the five-coordinate intermediates of base hydrolysis survive long enough to rearrange. Note that both *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{LX}]^{n+}$  often display similar reactivities in base hydrolysis—in contrast to acid hydrolysis, where the *cis* complexes are more reactive. Further evidence supporting this view lies in the stereochemical course of base hydrolysis discussed in Section 11.3.6.

Although steric effects of nonleaving ligands have not been investigated as intensively as for aquation, base hydrolysis rates for  $[\text{M}(\text{NH}_2\text{Me})_5(\text{OSO}_2\text{CF}_3)]^{2+}$  ( $\text{M}^{\text{III}} = \text{Co}, \text{Rh}, \text{Ir}, \text{Cr}$ ) were enhanced by a factor of  $>1000$  for Co, 150 for Rh, and 800 for Cr compared to the  $\text{NH}_3$  complexes. In contrast, only small enhancements were seen for acid hydrolysis for Co and Rh, and a small retardation was seen for Cr.<sup>22</sup>

### Product Analysis

If a five-coordinate intermediate exists, it must be able to discriminate among various entering groups (Section 11.3.4). In aqueous solution in the presence of  $\text{Y}^-$  the intermediate could be captured either by  $\text{Y}^-$  or by  $\text{H}_2\text{O}$ .



The percent of the intermediate captured by  $\text{Y}^-$  (obtained from separation and isolation of products) should depend on the nature of  $\text{Y}^-$  and should be the same, no matter how  $[\text{Co}(\text{NH}_3)_5(\text{NH}_2)]^{2+}$  is generated. Data in Table 11.17 give percents of *S*- and *N*-bonded thiocyanate products for base hydrolysis of several  $\text{Co}^{\text{III}}$  complexes in the presence of

**Table 11.17 Thiocyanate ion competition results for base hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$  at 25°C<sup>a</sup>**

$n+$	X	% <i>S</i> -isomer	% <i>N</i> -isomer	Total % thiocyanate
3+	OP(OMe) <sub>3</sub>	12.3	5.19	17.5
3+	OSMe <sub>2</sub>	12.0	5.93	17.9
2+	I <sup>-</sup>	8.90	4.69	13.6
2+	OSO <sub>2</sub> CF <sub>3</sub> <sup>-</sup>	8.88	4.62	13.4
2+	OSO <sub>2</sub> CH <sub>3</sub> <sup>-</sup>	8.68	4.70	13.4
1+	OSO <sub>3</sub> <sup>2-</sup>	3.7	3.1	6.8

<sup>a</sup>W. G. Jackson and C. N. Hookey, *Inorg. Chem.* **1984**, 23, 668.

<sup>22</sup>N. J. Curtis, G. A. Lawrance, P. A. Lay, and A. M. Sargeson, *Inorg. Chem.* **1986**, 25, 484.

NaSCN. All complexes studied were found to give a ratio of  $2.0 \pm 0.1$  *S*-isomer : *N*-isomer.<sup>23</sup> The total percent captured by  $\text{NCS}^-$  is constant for complexes of a particular charge and decreases with increasing negative charge on X. This is consistent with formation of a five-coordinate intermediate in which more-negative ligands remain in the second coordination sphere for a longer time, thus preventing capture by another negative ligand ( $\text{NCS}^-$ ). *The course of the base hydrolysis in the presence of competing ions differs from reactions in acid solution where  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$  first undergo aquation, then anation.*

### Proton Exchange

In the Garrick **D–CB** mechanism, hydroxide simply acts to deprotonate the starting complex to the more labile conjugate base (see problem 11.10). Hydroxide as the lyate ion of the solvent is the strongest base that can exist in aqueous solution and thus is uniquely effective. Base-catalyzed proton exchange between ammine ligands and solvent water has been amply demonstrated with the protons *trans* to X in  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$  exchanging more rapidly than those *cis* to it. The other possibility, that  $\text{OH}^-$  is the best entering group and nucleophile (which would support interpretation of the result via an **A** mechanism), has been ruled out in a classic labeling experiment.<sup>24</sup> Other evidence against  $\text{OH}^-$  as an entering group includes competition experiments<sup>25</sup> with  $\text{HO}_2^-$  and reactions in nonaqueous solvents containing added  $\text{OH}^-$ .<sup>26</sup>

### Activation Parameters

As might be expected if a five-coordinate intermediate is formed,  $\Delta V^\ddagger$  and  $\Delta S^\ddagger$  have been found to be large and positive for base hydrolysis. For a large number of  $\text{Co}^{\text{III}}$  complexes, there is also a linear relationship between  $\ln k_{\text{OH}}$  and  $\ln k_{\text{H}}$ , the rate constant for acid hydrolysis. This also means, of course, that  $\Delta G_{\text{OH}}^\ddagger$  is proportional to  $\Delta G_{\text{H}}^\ddagger$ , suggesting a common (**d**) mechanism. In contrast, no such relationship exists for Cr ammine complexes. This is interpreted to mean that for  $\text{Cr}^{\text{III}}$ , acid hydrolysis is **I**, whereas base hydrolysis is **D**.  $\text{Cr}^{\text{III}}$  complexes undergo base hydrolysis around 3300 times slower than their  $\text{Co}^{\text{III}}$  counterparts. This may result from lower acidity of the ligand protons or reduced reactivity of the five-coordinate intermediate.

In summary, base hydrolysis in complexes with acidic protons occurs via a **D–CB** mechanism involving a five-coordinate trigonal-bipyramidal intermediate. Water, rather than  $\text{OH}^-$ , is the entering group.

**EXAMPLE 11.2:** Some volumes of activation for base hydrolysis are given below. Rationalize the trends observed. (See Y. Kitamura, G. A. Lawrance, and R. van Eldik, *Inorg. Chem.* **1989**, *28*, 333.)

<sup>23</sup> W. G. Jackson and C. N. Hookey, *Inorg. Chem.* **1984**, *23*, 668.

<sup>24</sup> M. Breen and H. Taube, *Inorg. Chem.*, **1963**, *2*, 948.

<sup>25</sup> R. G. Pearson and D. N. Edgington, *J. Am. Chem. Soc.* **1962**, *84*, 4607.

<sup>26</sup> R. G. Pearson, H. H. Schmidtke, and F. Basolo, *J. Am. Chem. Soc.* **1960**, *82*, 4434.