Catálisis Ácido Base

$$k_{exp} = k_0 + k_H [H^+] + k_{OH} [OH^-] + k_A [A^-] + k_{HA} [HA]$$

Catálisis ácido- base general

Forma ácida y básica del solvente

Componentes del buffer usado

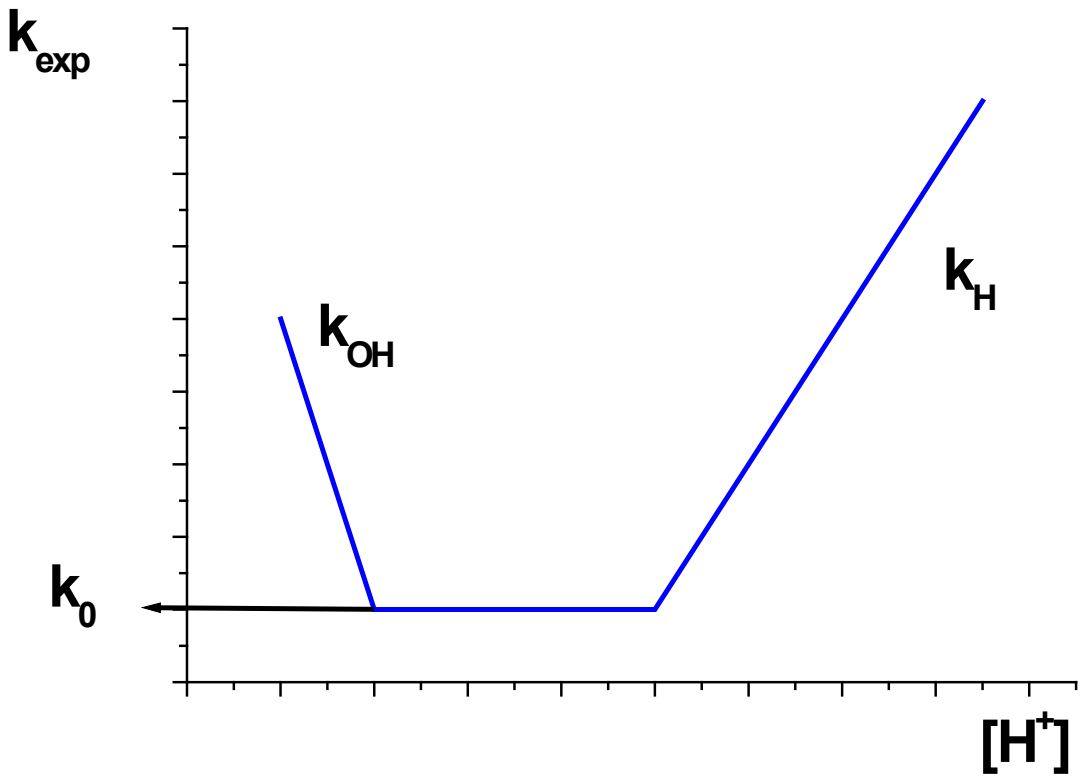
$$k_{exp} = k_0 + k_H [H^+] + k_{OH} [OH^-]$$

Catálisis ácido- base específica

No depende de la naturaleza ni la conc. del buffer empleado

$k_{exp} = k_0 + k_H [H^+]$ **Catálisis ácida específica**

$k_{exp} = k_0 + k_{OH} [OH^-]$ **Catálisis básica específica**



$$k_{exp} = k_0 + k_H[H^+] + \frac{k_{OH}K_w}{[H^+]}$$

Para estudios de catálisis ácido – base primero se trabaja con ácidos y bases fuertes para determinar si existe catálisis ácido-base específica.

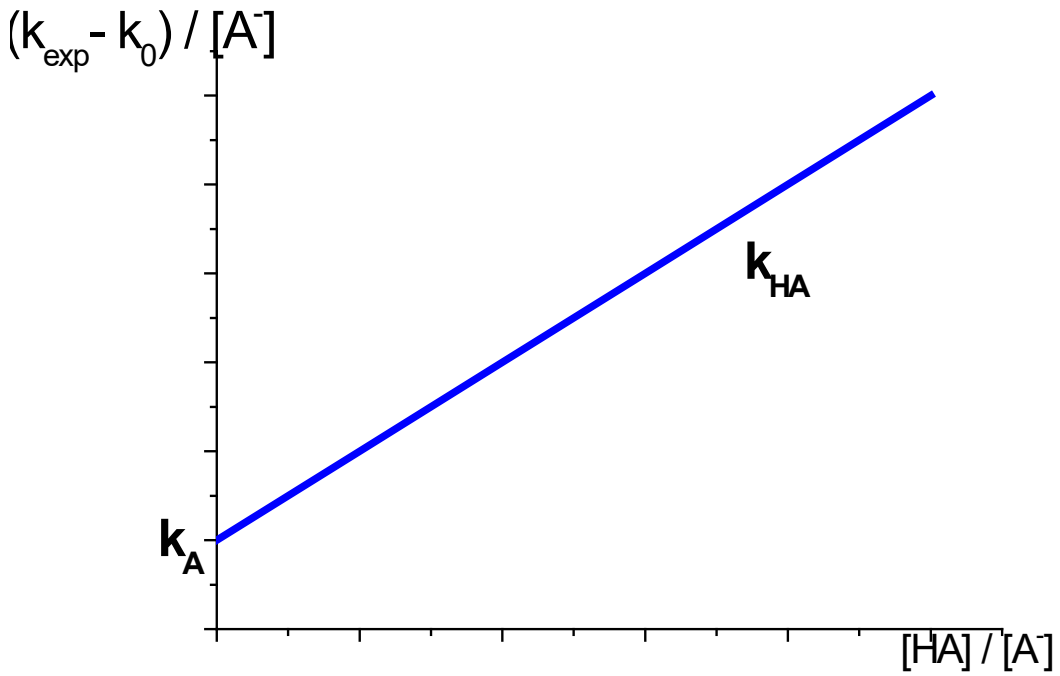
Ácido fuerte → k_H

Base fuerte → k_{OH}

El paso siguiente es ver si existe catálisis acido base general.

Para determinar la influencia de la concentración del buffer empleado, se puede trabajar en la región de pH en la cual no hay catálisis específica => $k_0 + k_H [H^+] + k_{OH} [OH^-] = k_0$

$$k_{exp} - k_0 = k_A [A^-] + k_{HA} [HA]$$



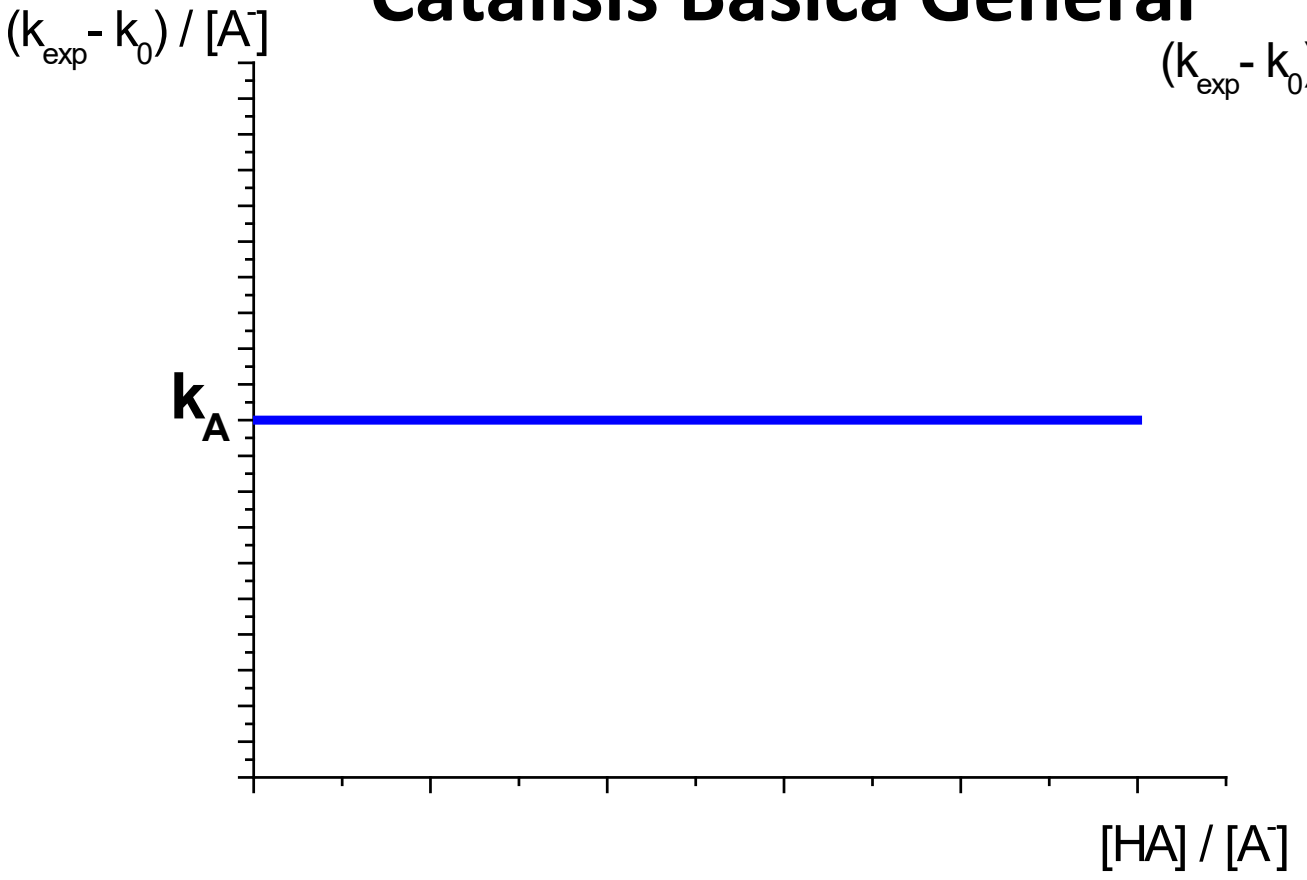
R

$$\frac{k_{exp} - k_0}{[A^-]} = k_A + k_{HA} \frac{[HA]}{[A^-]}$$

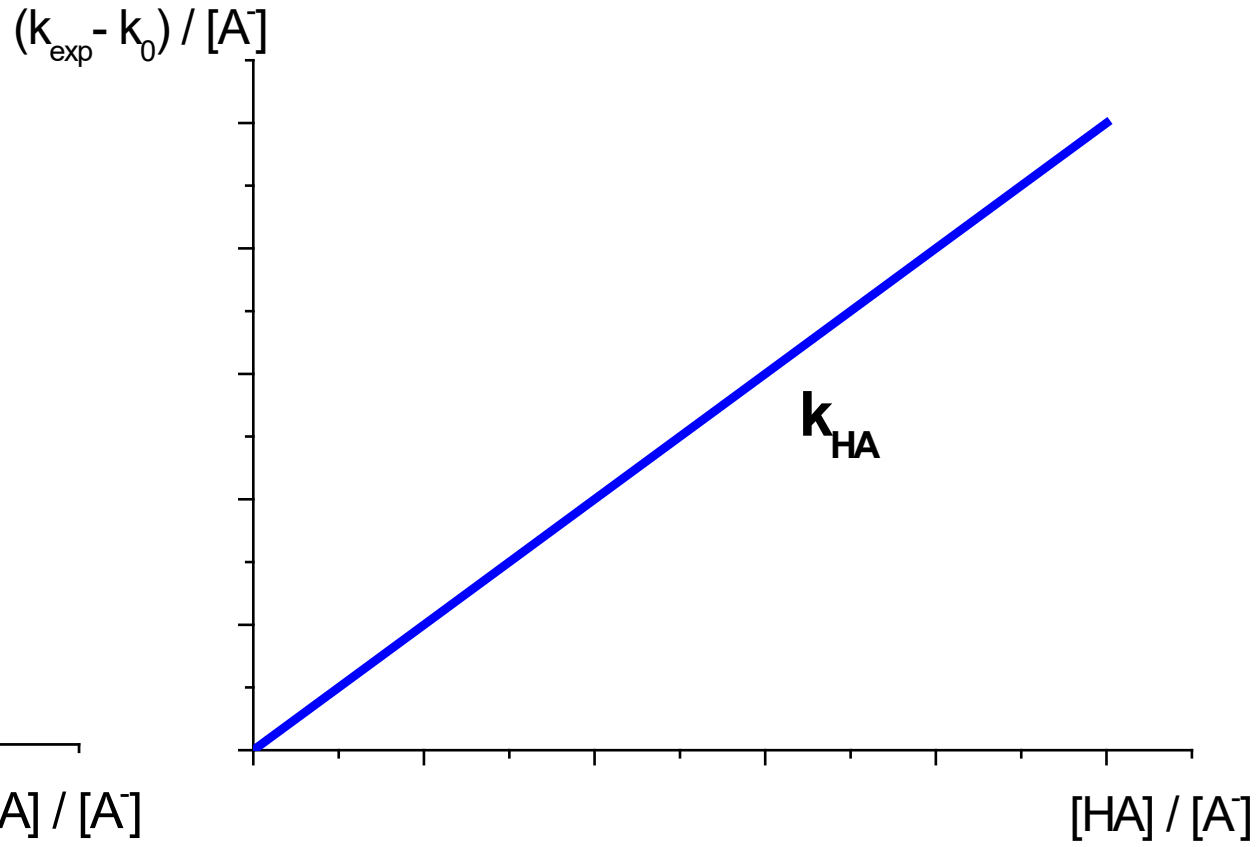
Catálisis Ácido Base General

$$\frac{k_{exp} - k_0}{[A^-]} = k_A + k_{HA}\frac{[HA]}{[A^-]}$$

Catálisis Básica General



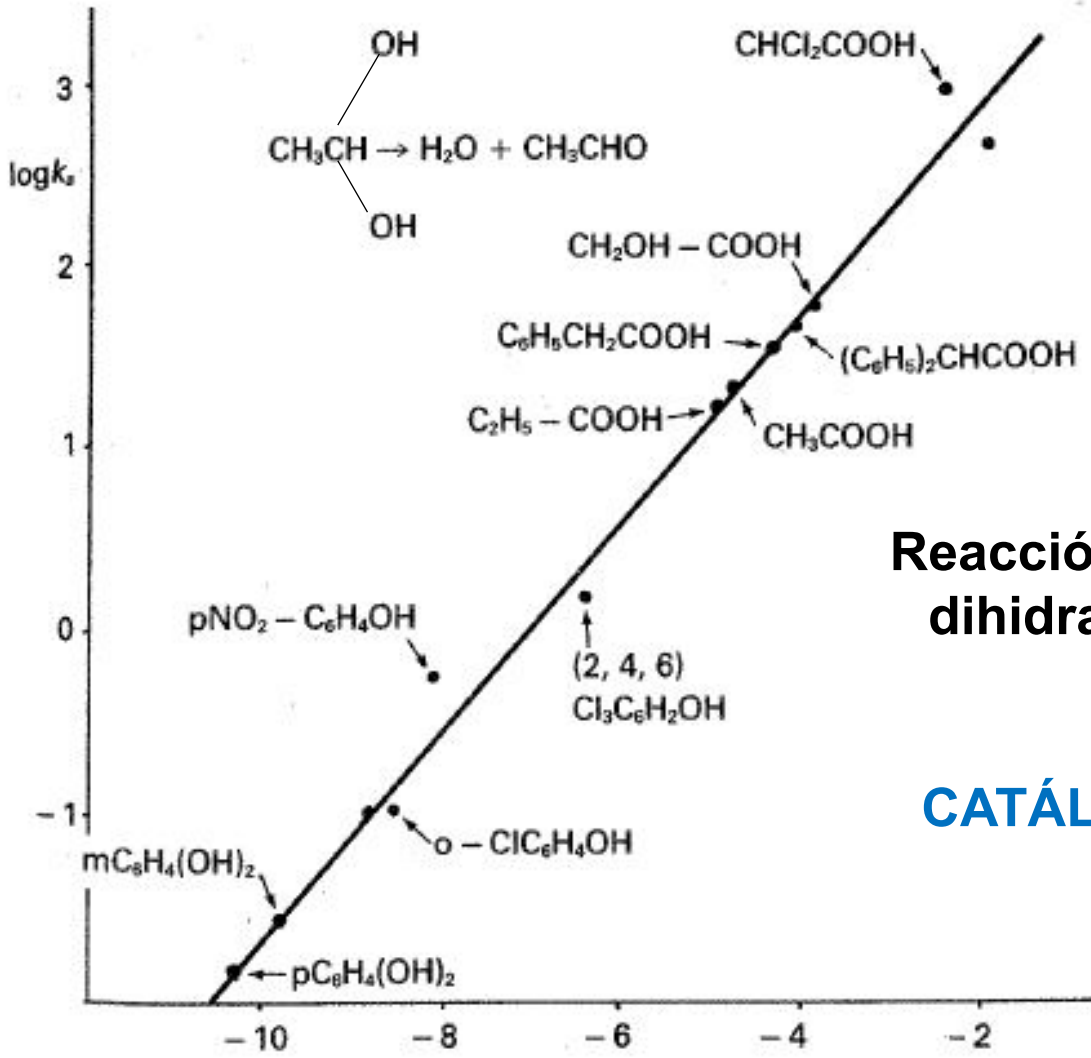
Catálisis Ácida General



Relación de Brønsted-Pedersen: REL para catálisis ácido/base general

$$\text{Log } k_{cat} = \log C_a + \alpha \log K_a$$

$$\text{Log } k_{cat} = \log C_b + \beta \log K_b$$



Reacción de deshidratación del dihidrato de acetaldehído en acetona

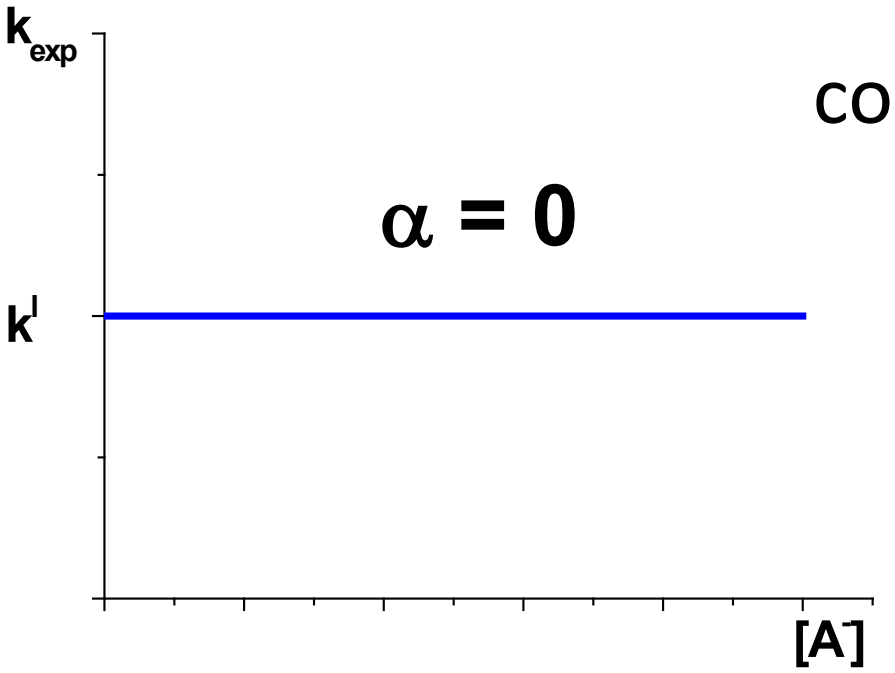
CATÁLISIS ÁCIDA GENERAL

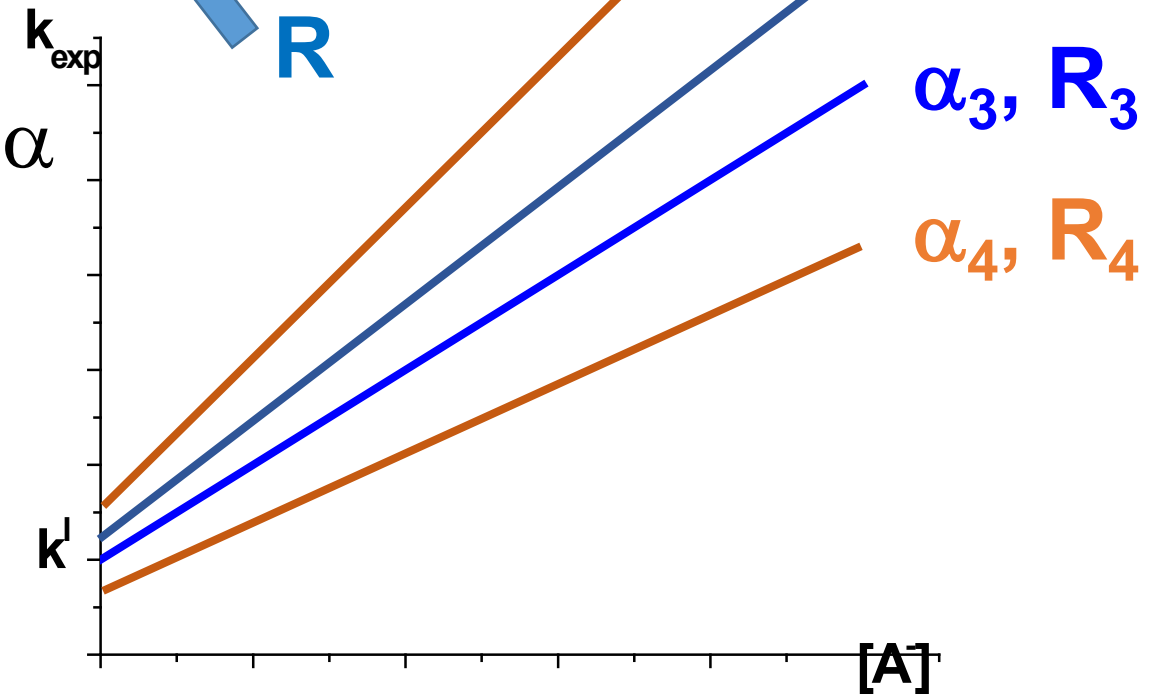
$$k_{exp} = k_0 + k_H [H^+] + k_{OH} [OH^-] + k_A [A^-] + k_{HA} [HA]$$

$$k_{exp} = k^l + \left(k_A + k_{HA} \frac{[HA]}{[A^-]} \right) [A^-]$$

R

constante = α

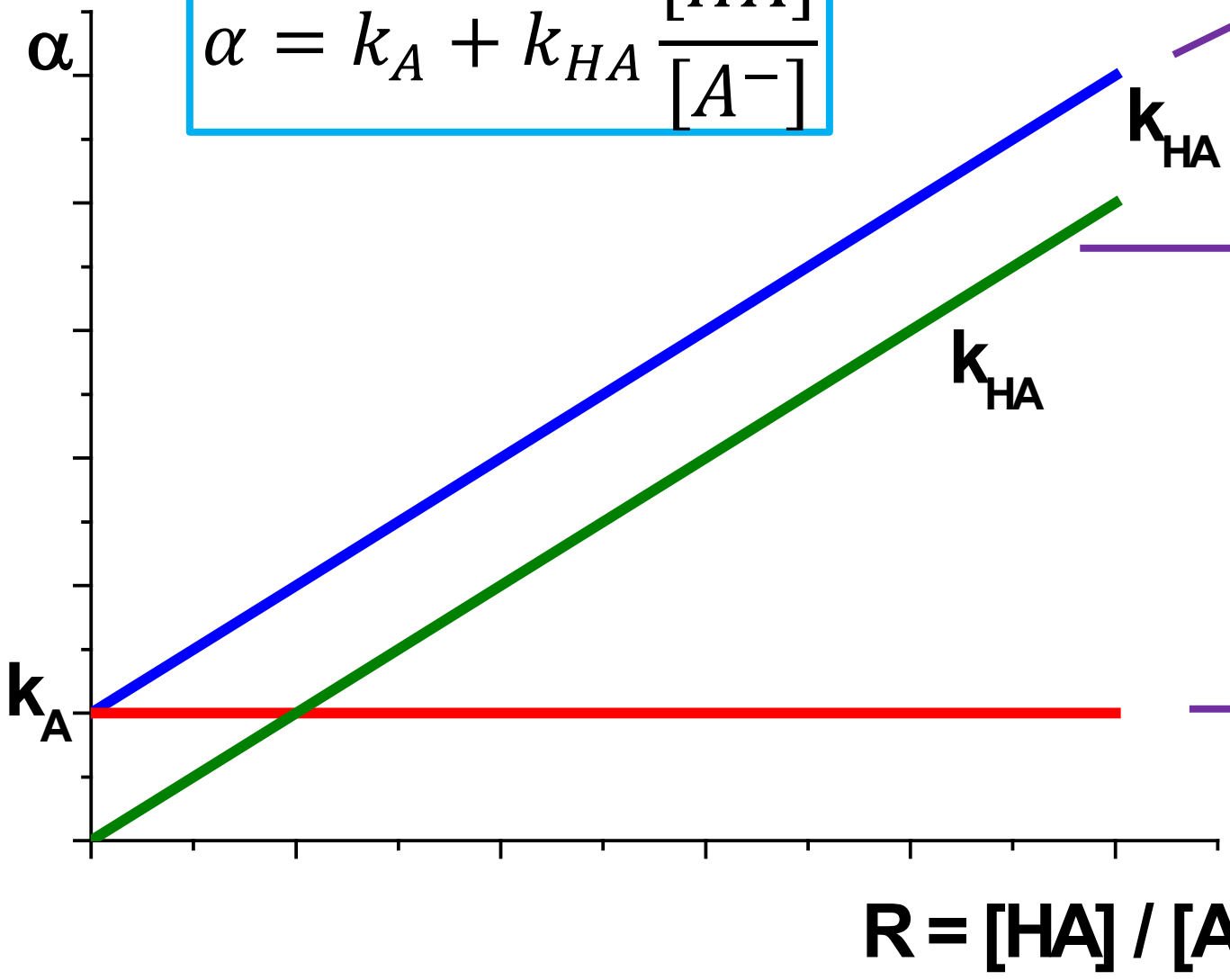




No hay catálisis ácido base general

Hay catálisis ácido base general

$$\alpha = k_A + k_{HA}\frac{[HA]}{[A^-]}$$

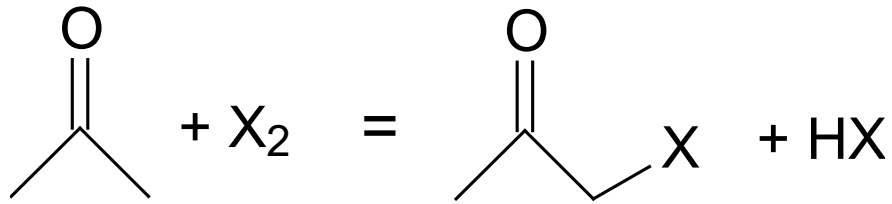


Catálisis ácido base general

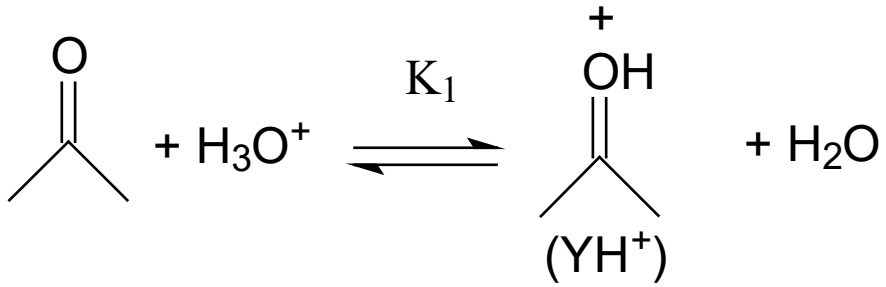
Catálisis ácida general

Catálisis básica general

En Medio Ácido => Catálisis Ácida General

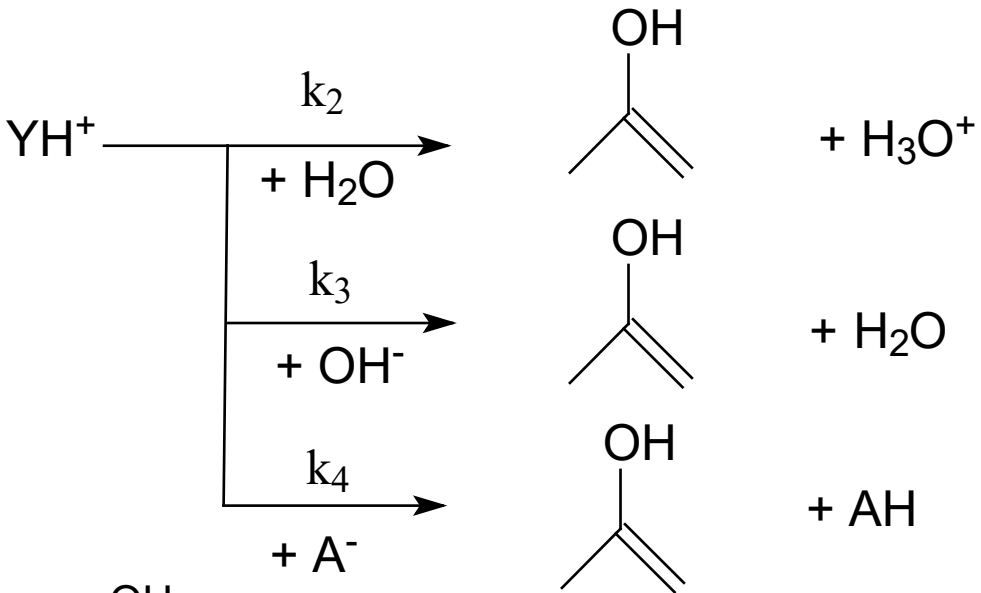


$v = k_{exp}[acetona]$; indep. X_2



$$v = k_2[YH^+] + k_3[YH^+][OH^-] + k_4[YH^+][A^-]$$

$$v = K_1[acetona][H^+](k_2 + k_3[OH^-] + k_4\,[A^-])$$



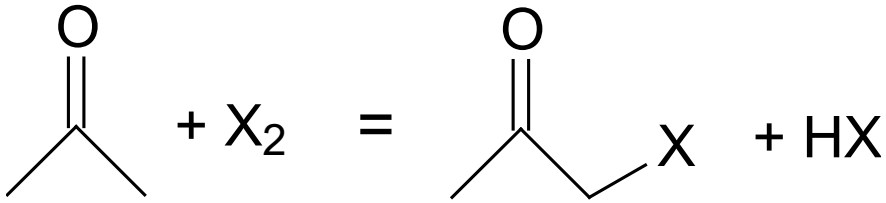
$$v = K_1[acetona]\,(k_2[H^+] + k_3K_w + k_4[H^+][A^-])$$

$$v = K_1[acetona]\,(k_2[H^+] + k_3K_w + k_4K_{AH}[AH])$$

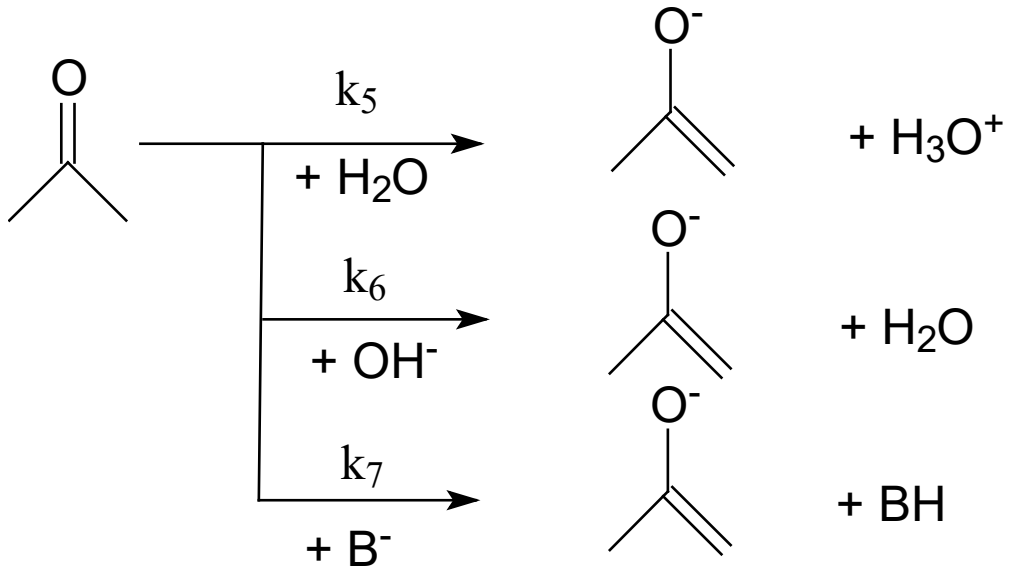
$$v = [acetona]\,(K_1k_2[H^+] + K_1k_3K_w + K_1k_4K_{AH}[AH])$$

$$\boldsymbol{v = (k_H[H^+] + k_0 + k_{AH}\,[AH])[acetona]}$$

En Medio Básico => Catálisis Básica General

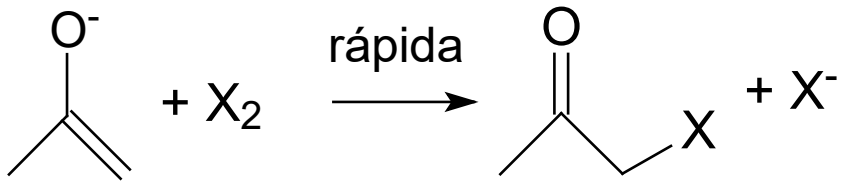


$v = k_{exp}[acetona]$; indep. X_2

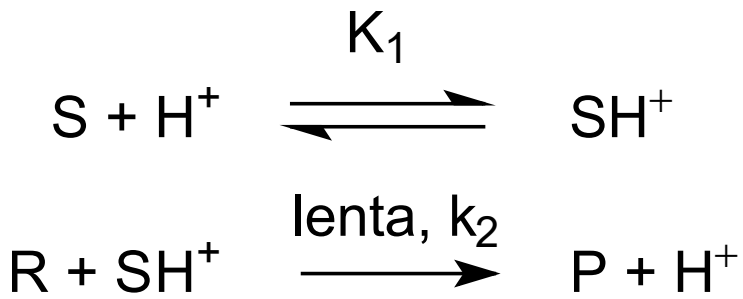


$$v = (k_5 + k_6[OH^-] + k_7\,[B^-])[acetona]$$

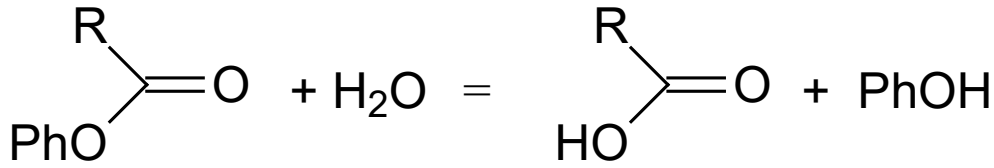
$$\boldsymbol{v = (k_0 + k_{OH}[OH^-] + k_B\,[B^-])[acetona]}$$

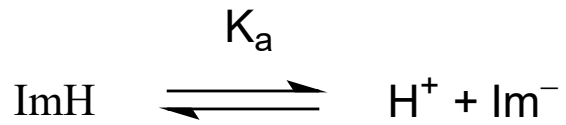


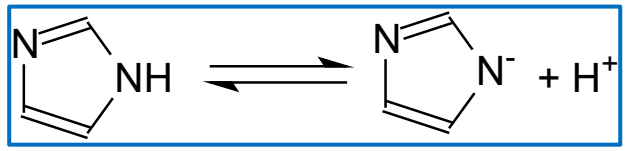
$$R + S = P$$

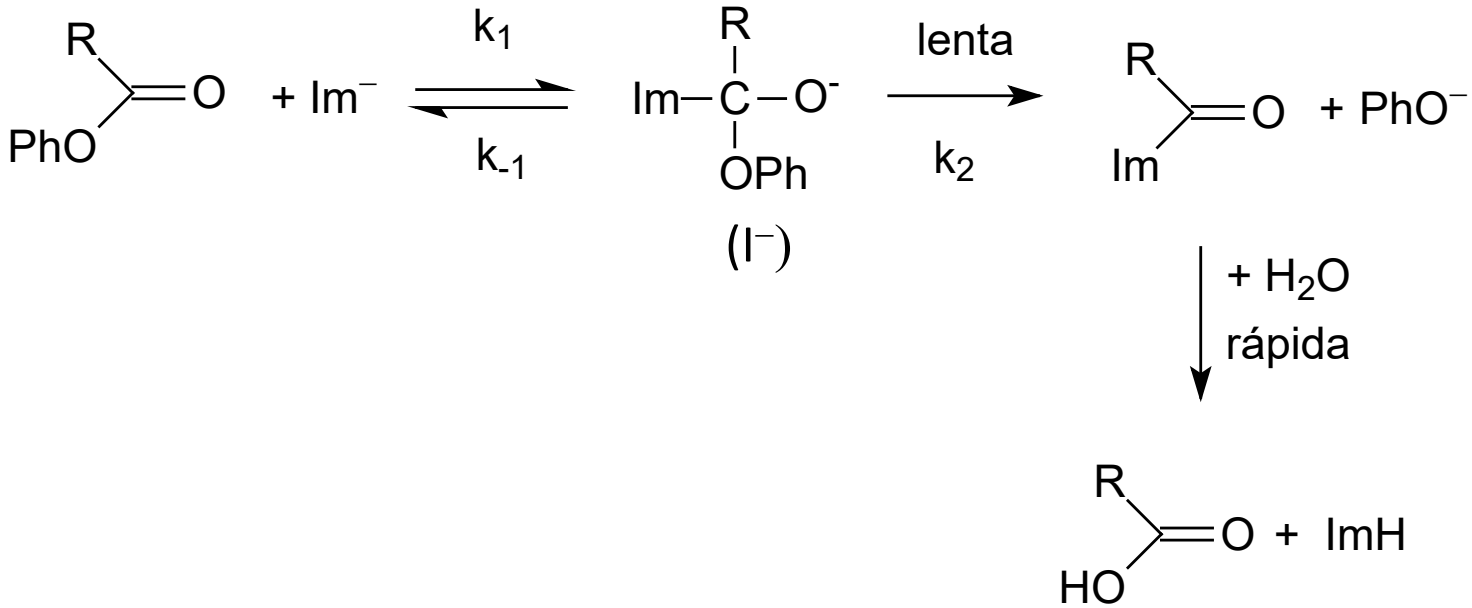


$$v = k_2 [R][SH^+] = k_2 K_1 [R][S][H^+]$$

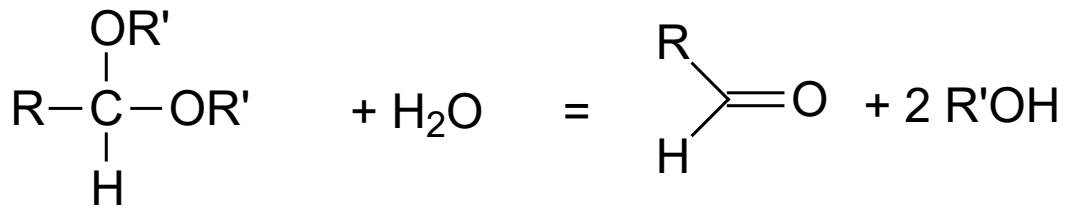


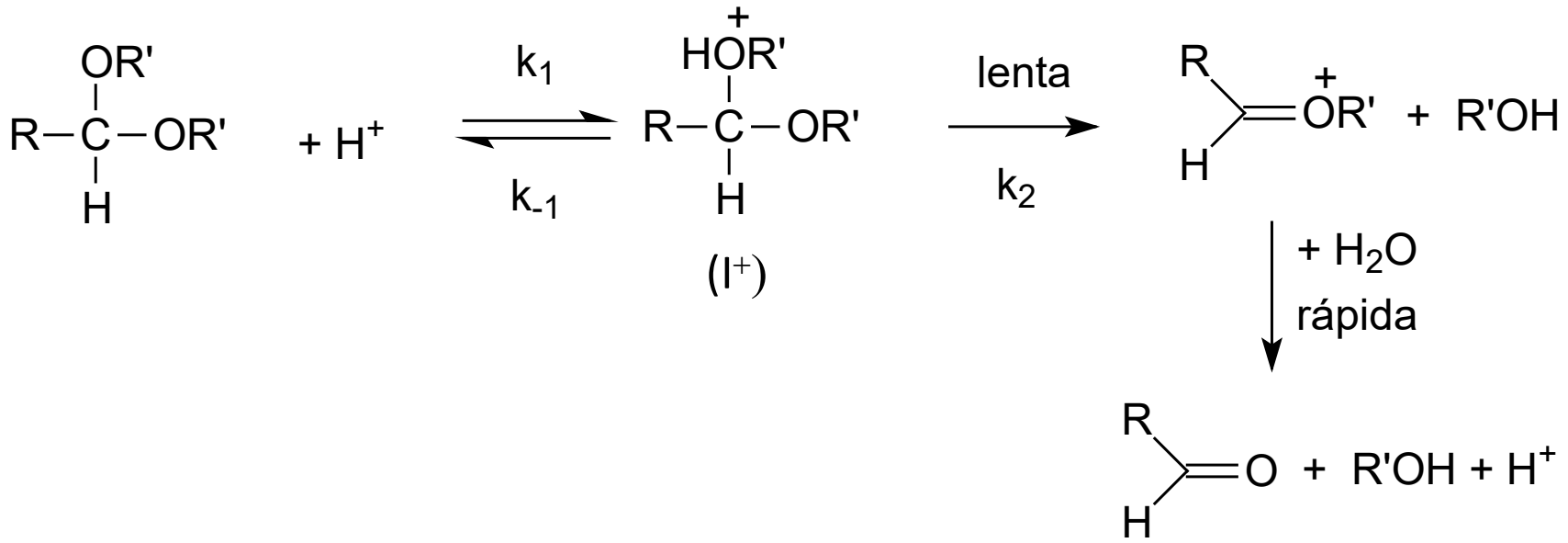




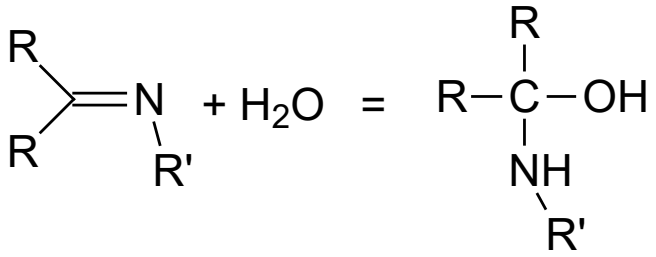


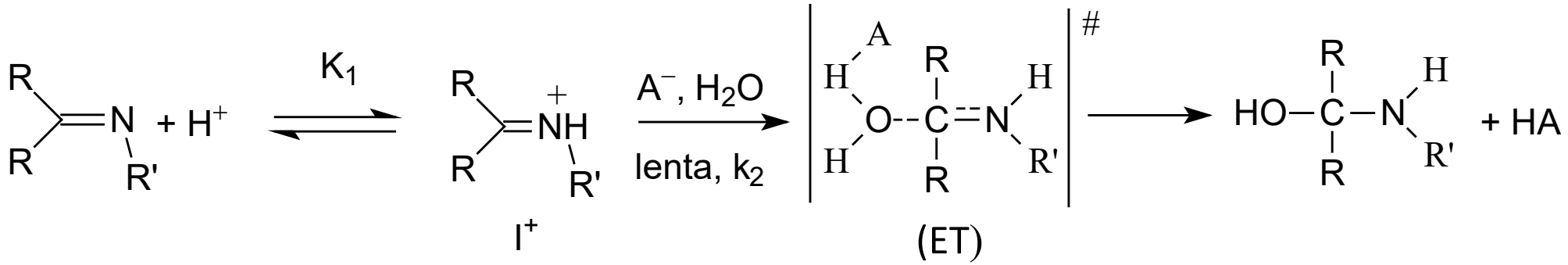
$$v = k_2 [I^-] = k_2 k_1 [\text{éster}][Im^-]/(k_{-1} + k_2) = k_2 k_1 Ka [\text{éster}][HIm]/[H^+](k_{-1} + k_2)$$

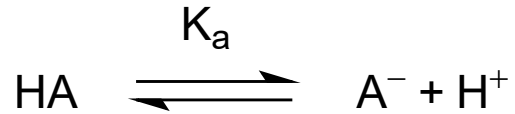




$$v = k_2 [I^+] = k_2 k_1 [\text{acetal}][H^+]/(k_{-1} + k_2)$$







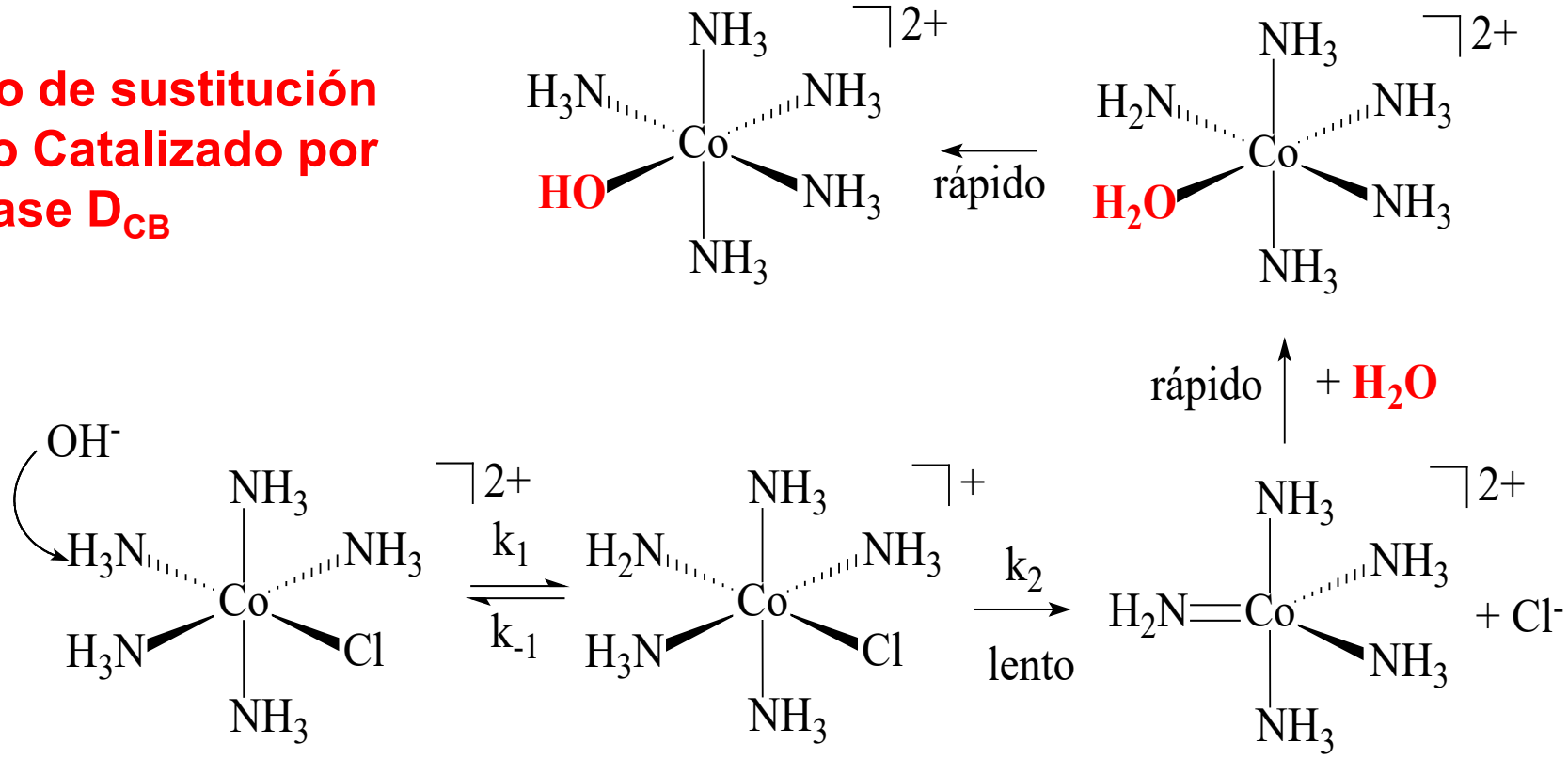
$$v = k_2 [I^+] [A^-] = k_2 K_1 [imina][H^+][A^-] = k_2 K_1 Ka [imina][HA]$$

$[Co(NH_3)_5Cl]^{2+} + OH^- = [Co(NH_3)_5OH]^{2+} + Cl^-$

Ley de velocidad

$$v = k_{OH}[Co(III)][OH^-]$$

Mecanismo de sustitución Disociativo Catalizado por base D_{CB}



Ley de velocidad a partir del mecanismo

$$v = nk_1k_2[Co(NH_3)_5L^{2+}][OH^-]/(k_{-1} + k_2)$$

n = nro de H^+ en el reactivo