Reactions: Classical and Organometallic Mechanisms



Water Exchange Rates



Timescale*	Process	Example
10 ⁸ s	Ligand exchange (inert complex)	$[Cr(OH_2)_6]^{3+} - H_2O(c. 6 days)$
60 s	Ligand exchange (nonlabile complex)	$[V(OH_2)_6]^{3+} - H_2O$ (50 s)
1 ms	Ligand exchange (labile complex)	$[Pt(OH_2)_4]^{2+} - H_2O$ (0.4 ms)
1 µs	Intervalence charge transfer	$(H_3N)_5Ru^{II} - N N - Ru^{III}(NH_3)$
		(0.5 µs)
1 ns	Ligand exchange (labile complex)	$[Ni(OH_2)_5(py)]^{2+} - H_2O(1 ns)$
10 ps	Ligand association	$Cr(CO)_5 + THF (10 ps)$
1 ps	Rotation time in liquid	CH ₃ CN (1 ps)
1 fs	Molecular vibration	Sn-Cl stretch (300 fs)

 Table 21.1
 Representative timescales of chemical and physical processes

* Approximate time at room temperature.

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Table 21.8 Activation parameters for the H_2O exchange reactions $[M(OH_2)_6]^{2+} + H_2^{17}O \rightarrow [M(OH_2)_5(^{17}OH_2)]^{2+} + H_2O$

	$\Delta^{\dagger}H/(kJ mol^{-1})$	LFSE*/ $\Delta_{\rm o}$	(LFSE) [‡] / Δ_0^{\dagger}	LFAE/ Δ_{0}	$\Delta^{\dagger}V/(\mathrm{cm}^{3} \mathrm{mol}^{-1})$
$Ti^{2+}(d^2)$		0.8	0.91	-0.11	
V ²⁺ (d ³)	68.6	1.2	1	0.2	-4.1
Cr ²⁺ (d ⁴ , hs)		0.6	0.91	-0.31	
Mn ²⁺ (d ⁵ , hs)	33.9	0	0	0	-5.4
$Fe^{2+}(d^{6}, hs)$	31.2	0.4	0.46	-0.06	+3.8
Co ²⁺ (d ⁷ , hs)	43.5	0.8	0.91	-0.11	+6.1
Ni ²⁺ (d ⁸)	58.1	1.2	1	0.2	+7.2

* Octahedral. + Square pyramidal. hs, high spin.

Typical form of reaction profile for dissociative mechanism



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Inorganic Chemistry Chapter 1: Figure 21.4





Trans Effect vs. Trans Influence

- Trans effect: A strong σ-donor or πacceptor ligand greatly accelerates substitution of a ligand that lies in the position trans to it.
- Trans Influence: Extent to which the ligand T weakens the bond trans to itself in the ground state of the complex. Correlates with σ-donating ability.

Ligand	$k_{r,obs} / (dm^3 \text{ mol}^{-1} \text{ s}^{-1})$	$K_{\rm E}/({\rm dm^3\ mol^{-1}})$	$(k_{r,obs}/K_E)/s^{-1}$
CH ₃ CO ₂ ⁻	1×10^{5}	3	3×10^{4}
F ⁻	8×10^{5}	1	8×10^{3}
HF	3×10^{3}	0.15	2×10^{4}
H ₂ O*			3×10^{3}
NH ₃	5×10^{3}	0.15	3×10^{4}
$[NH_2(CH_2)_2NH_3]^+$	4×10^{2}	0.02	2×10^{4}
SCN ⁻	6×10^{3}	1	6×10^{3}

Table 21.6 Complex formation by the $[Ni(OH_2)_6]^{2+}$ ion

* The solvent is always in encounter with the ion so that $K_{\rm E}$ is undefined and all rates are inherently first order.

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