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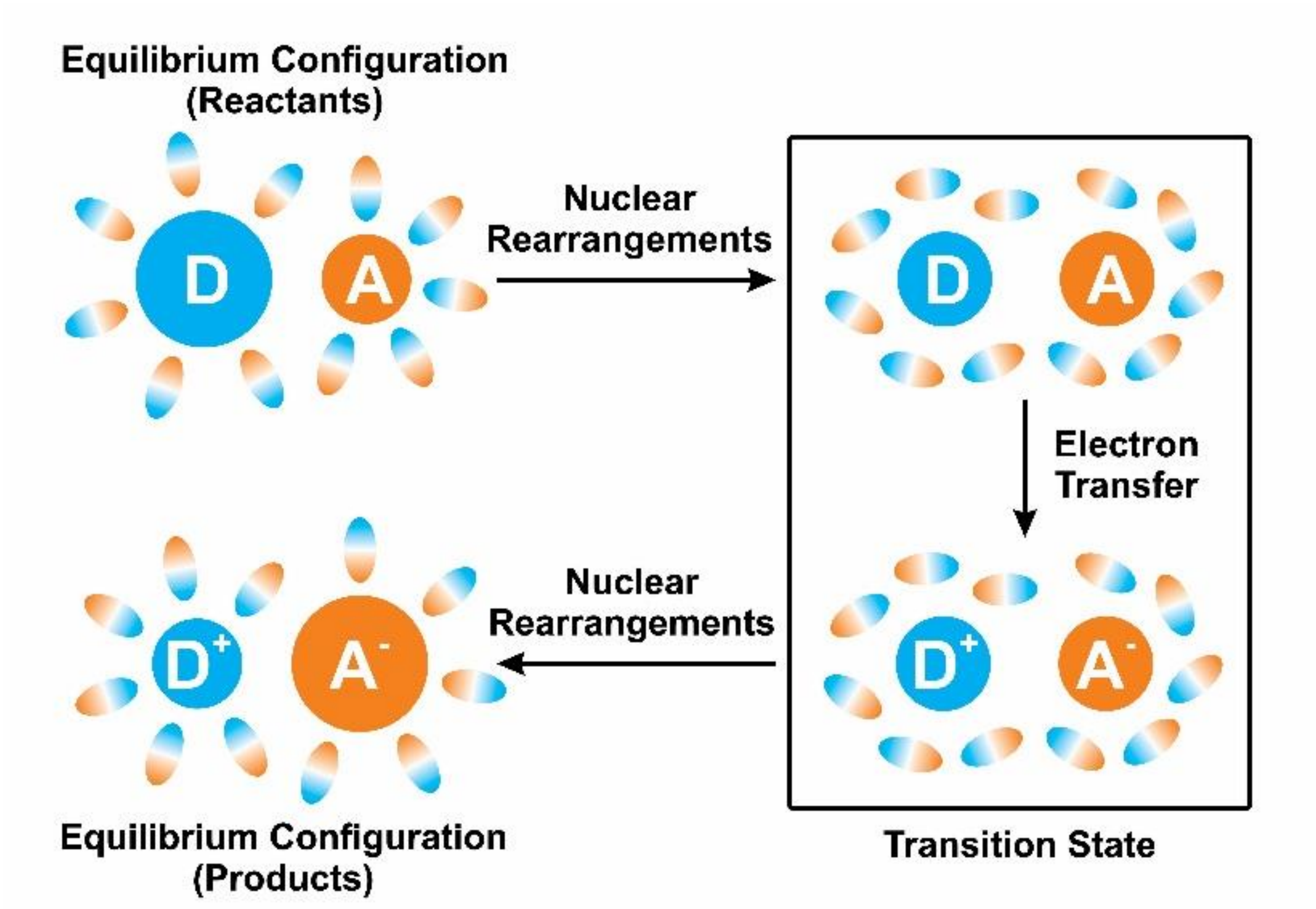
Cinética de transferência eletrônica

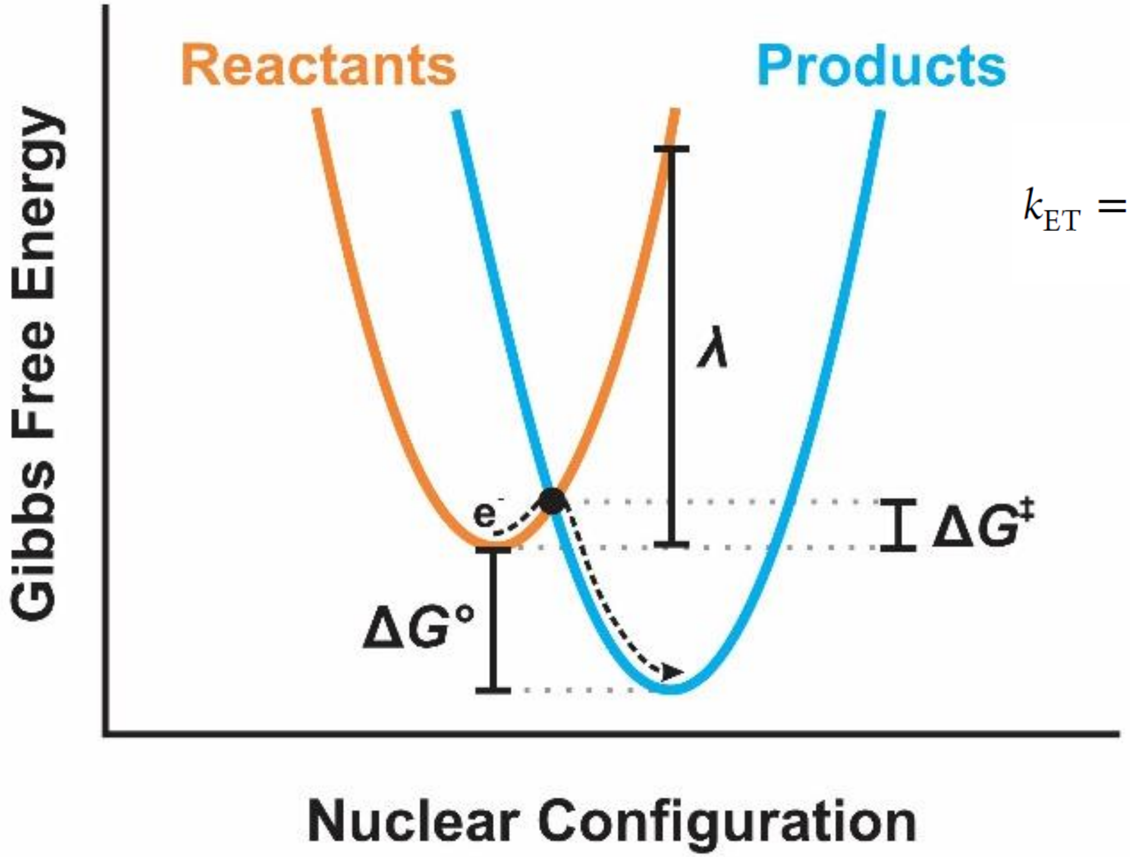
Mecanismo de esfera interna

Bridging ligand, X	k / dm^3 mol^{-1} s^{-1}
F^-	2.5×10^5
Cl^-	6.0×10^5
Br^-	1.4×10^6
I^-	3.0×10^6
$[N_3]^-$	3.0×10^5
$[OH]^-$	1.5×10^6
H_2O	0.1

Mecanismo de esfera externa - Modelo



Müller, A.; Wierzba, W.; Pastorelli, M.; Polo, A. S., Interfacial Electron Transfer in Dye-Sensitized TiO_2 Devices for Solar Energy Conversion. *J. Braz. Chem. Soc.* **2021**, *32* (9), 1711-1738.



$$k_{ET} = \frac{2\pi}{\hbar}\frac{{H_{DA}}^2}{\sqrt{4\pi\lambda k_b T}}\exp\left(-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_b T}\right)$$

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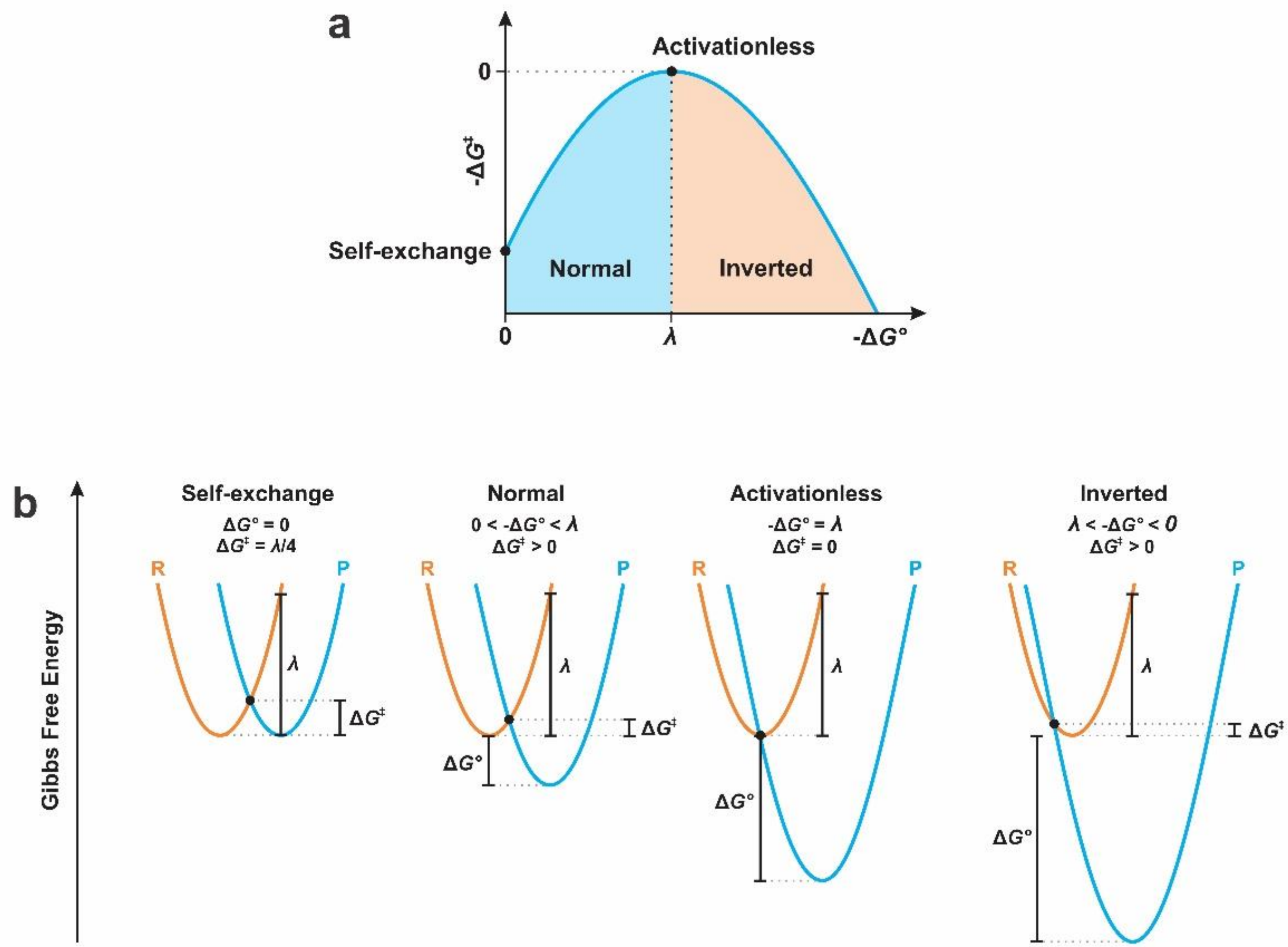
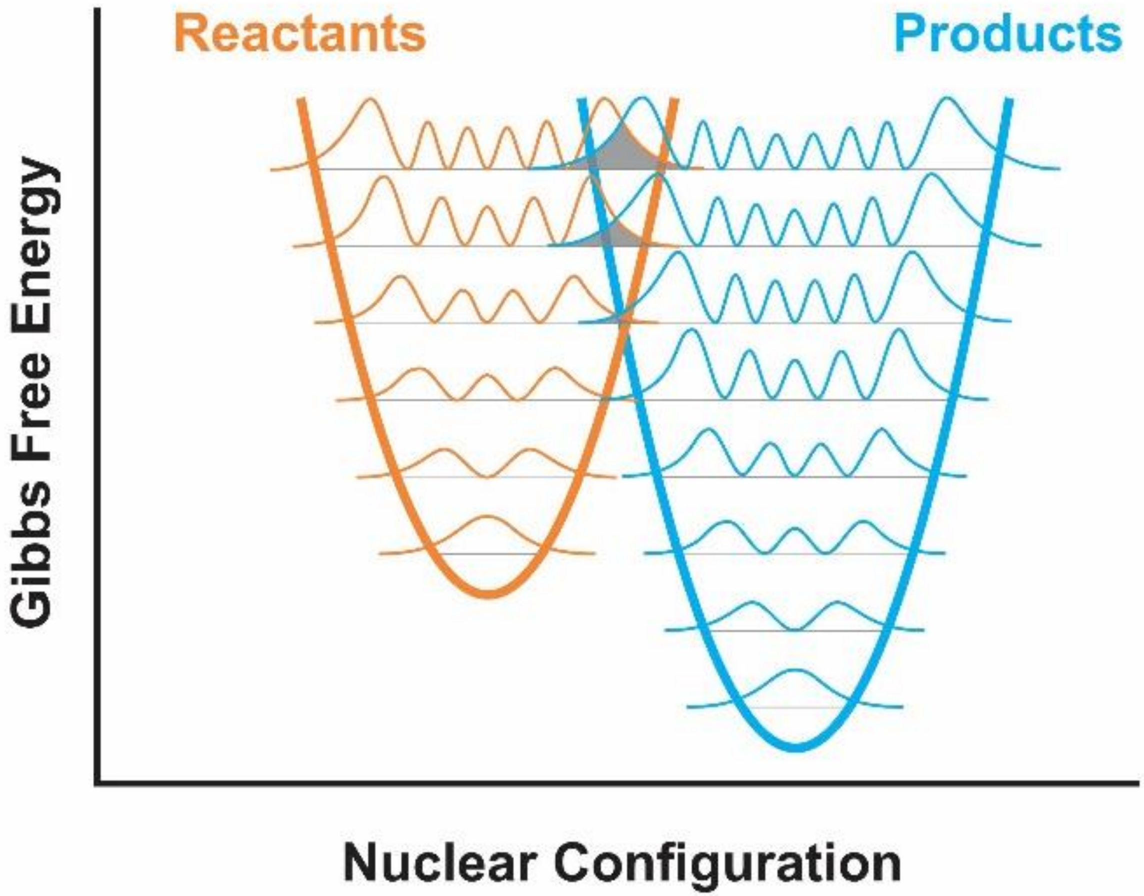


Müller, A.; Wierzba, W.; Pastorelli, M.; Polo, A. S., Interfacial Electron Transfer in Dye-Sensitized TiO_2 Devices for Solar Energy Conversion. *J. Braz. Chem. Soc.* **2021,** *32* (9), 1711-1738.



Müller, A.; Wierzba, W.; Pastorelli, M.; Polo, A. S., Interfacial Electron Transfer in Dye-Sensitized TiO_2 Devices for Solar Energy Conversion. *J. Braz. Chem. Soc.* **2021,** *32* (9), 1711-1738.

Algumas reações de auto-troca

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Reação	k / $M^{-1}s^{-1}$
$[Os(bpy)_3]^{2+} + [Os(bpy)_3]^{3+} \longrightarrow [Os(bpy)_3]^{3+} + [Os(bpy)_3]^{2+}$	$> 10^6$
$[Fe(bpy)_3]^{2+} + [Fe(bpy)_3]^{3+} \longrightarrow [Fe(bpy)_3]^{3+} + [Fe(bpy)_3]^{2+}$	$> 10^6$
$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$	3
$[Co(phen)_3]^{2+} + [Co(phen)_3]^{3+} \longrightarrow [Co(phen)_3]^{3+} + [Co(phen)_3]^{2+}$	40
$[Co(en)_3]^{2+} + [Co(en)_3]^{3+} \longrightarrow [Co(en)_3]^{3+} + [Co(en)_3]^{2+}$	10^{-4}
$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \longrightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$	10^{-6}
$[Ru(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+} \longrightarrow [Ru(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{2+}$	$8,2 \times 10^2$

Conjugação do ligante

Configuração eletrônica do metal

Pouca variação no comprimento de ligação

Verificando se é TE esfera externa

Reação	k / $M^{-1}s^{-1}$
$[Os(bpy)_3]^{2+} + [Os(bpy)_3]^{3+} \longrightarrow [Os(bpy)_3]^{3+} + [Os(bpy)_3]^{2+}$	$> 10^6$
$[Fe(bpy)_3]^{2+} + [Fe(bpy)_3]^{3+} \longrightarrow [Fe(bpy)_3]^{3+} + [Fe(bpy)_3]^{2+}$	$> 10^6$
$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$	3
$[Co(phen)_3]^{2+} + [Co(phen)_3]^{3+} \longrightarrow [Co(phen)_3]^{3+} + [Co(phen)_3]^{2+}$	40
$[Co(en)_3]^{2+} + [Co(en)_3]^{3+} \longrightarrow [Co(en)_3]^{3+} + [Co(en)_3]^{2+}$	10^{-4}
$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \longrightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$	10^{-6}
$[Ru(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+} \longrightarrow [Ru(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{2+}$	$8,2 \times 10^2$

$[Ru(NH_3)_6]^{2+} + [Co(phen)_3]^{3+} \longrightarrow [Ru(NH_3)_6]^{3+} + [Co(phen)_3]^{2+}$

$K_{eq} = 2,6 \times 10^5$

$$k_{12} = (k_{11}k_{22}K_{eq}f)^{1/2}$$

$$\ln(f_{12}) = \frac{\ln(K_{eq})^2}{4\ln\left(\frac{k_{11}k_{22}}{Z^2}\right)}$$

Calculado

$k_{12} = 1 \times 10^4\ M^{-1}s^{-1}$

Experimental

$k_{12} = 1,5 \times 10^4\ M^{-1}s^{-1}$

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Table 13.8

Calculated and observed rate constants for outer sphere cross reactions[a]

Reaction	log K_{12}	k_{12obsd} (M^{-1} s^{-1})	$k_{12calcd}$ (M^{-1} s^{-1})
$Ru(NH_3)_6^{2+}$ + $Ru(NH_3)_5py^{3+}$	4.40	1.4×10^6	4×10^6
$Ru(NH_3)_5py^{2+}$ + $Ru(NH_3)_4(bpy)^{3+}$	3.39	1.1×10^8	4×10^7
$Ru(NH_3)_6^{2+}$ + $Co(phen)_3^{3+}$	5.42	1.5×10^4	1×10^5
$Ru(NH_3)_5py^{2+}$ + $Co(phen)_3^{3+}$	1.01	2.0×10^3	1×10^4
V_{aq}^{2+} + $Co(en)_3^{3+}$	0.25	5.8×10^{-4}	7×10^{-4}
V_{aq}^{2+} + $Ru(NH_3)_6^{3+}$	5.19	1.3×10^3	1×10^3
V_{aq}^{2+} + Fe_{aq}^{3+}	16.90	1.8×10^4	2×10^6
Fe_{aq}^{2+} + $Os(bpy)_3^{3+}$	1.53	1.4×10^3	5×10^5
Fe_{aq}^{2+} + $Fe(bpy)_3^{3+}$	3.90	2.7×10^4	6×10^6
$Ru(NH_3)_6^{2+}$ + Fe_{aq}^{3+}	11.23	3.4×10^5	2×10^6
$Ru(en)_3^{2+}$ + Fe_{aq}^{3+}	9.40	8.4×10^4	4×10^5
$Mo(CN)_8^{4-}$ + $IrCl_6^{2-}$	2.18	1.9×10^6	8×10^5
$Mo(CN)_8^{4-}$ + MnO_4^-	−4.07	2.7×10^2	6×10^1
$Mo(CN)_8^{4-}$ + $HMnO_4$	8.48	1.9×10^7	2×10^7
$Fe(CN)_6^{4-}$ + $IrCl_6^{2-}$	4.08	3.8×10^5	1×10^6
$Fe(CN)_6^{4-}$ + $Mo(CN)_8^{3-}$	2.00	3.0×10^4	4×10^4
$Fe(CN)_6^{4-}$ + MnO_4^-	3.40	1.7×10^5	6×10^4

[a] Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

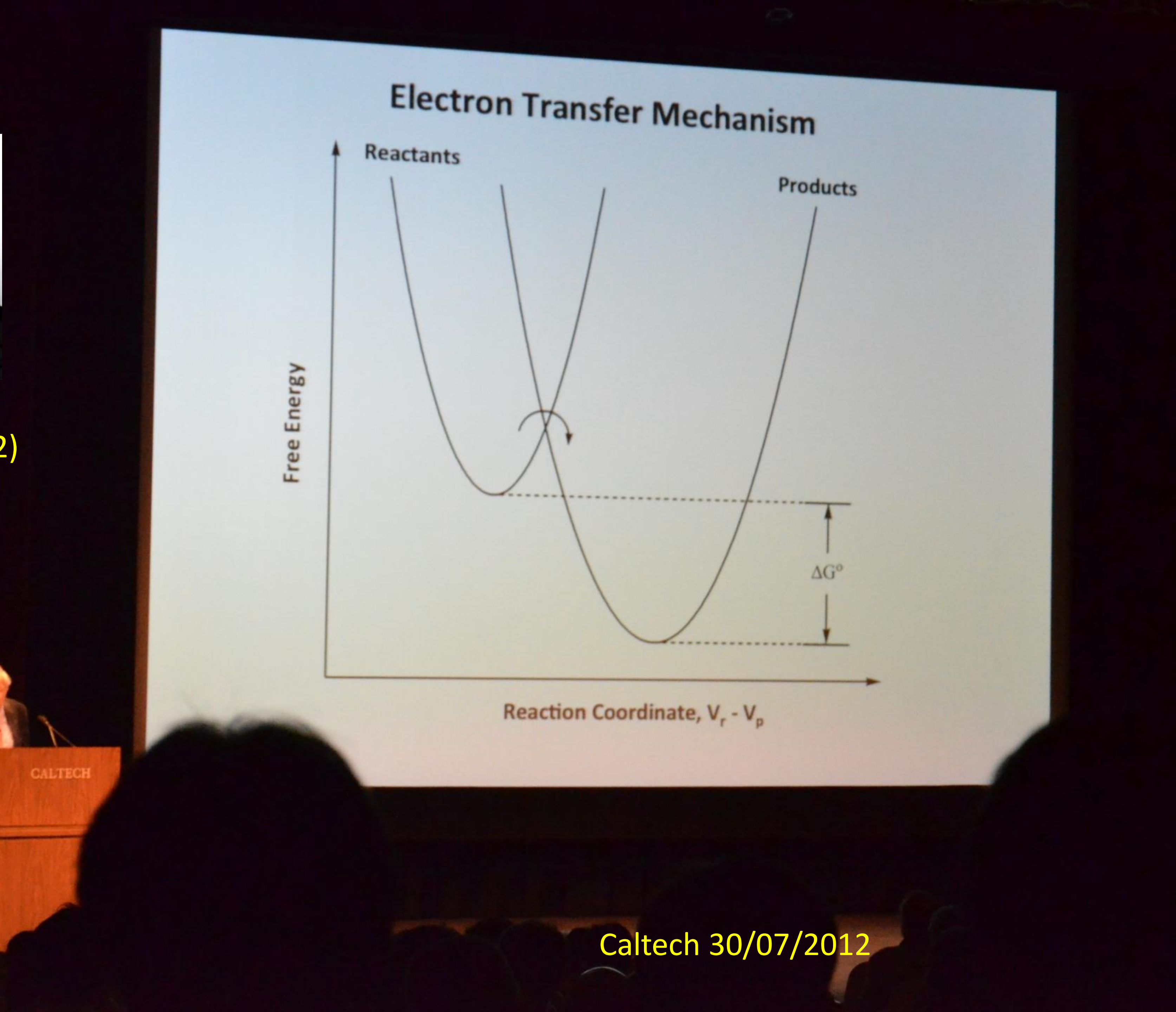
Considerações sobre a teoria de Marcus

1. Alta confiança na teoria
   – Caso $k_{12\ calcd} \neq k_{12expttal}$ verificar se outro mecanismo não está ocorrendo.

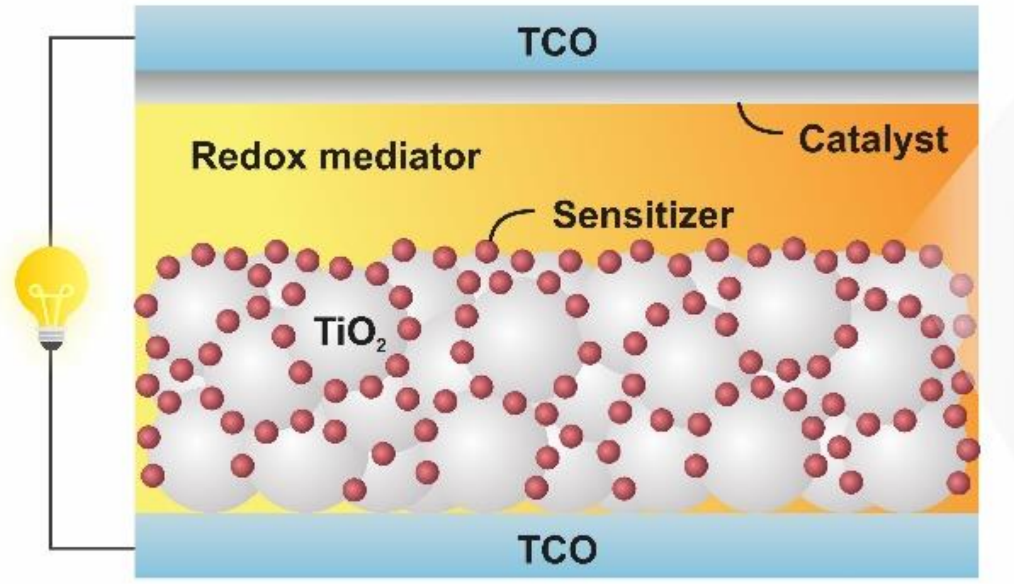
2. Teoria de Marcus conecta a cinética e a termodinâmica
   – k_{12} aumenta diretamente com K_{12}

3. Este é apenas um pedaço da teoria

R. Marcus
Nobel (1992)



Caltech 30/07/2012


TCO
Catalyst
Redox mediator
Sensitizer
TiO_2
TCO

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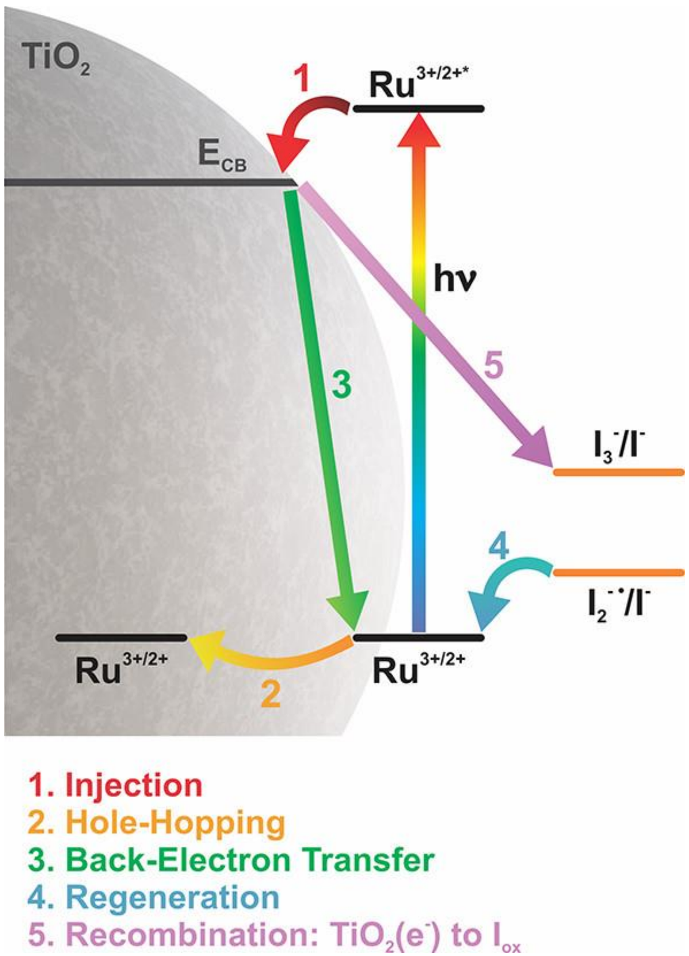
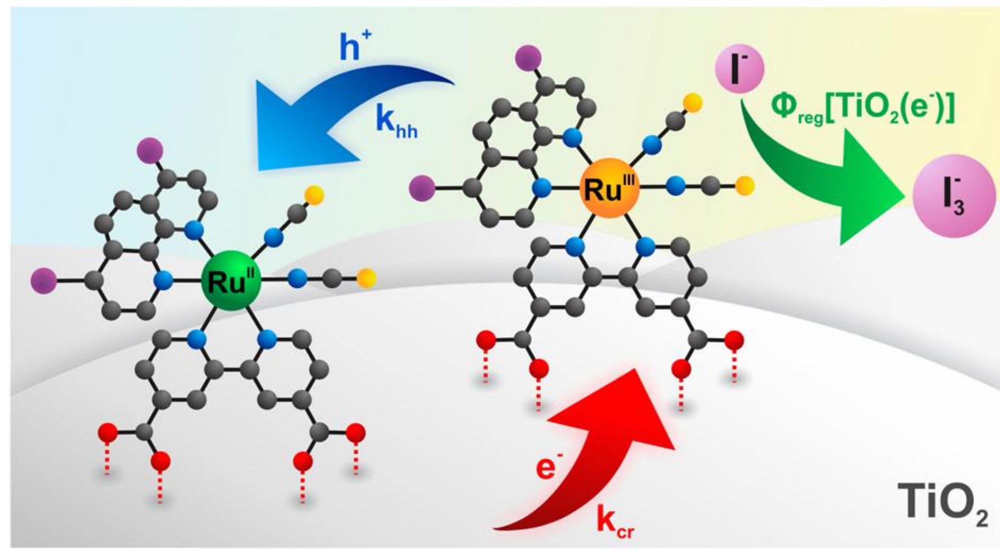
Estudo de caso

*Müller, A. V.; de Oliveira, K. T.; Meyer, G. J.; Polo, A. S., Inhibiting Charge Recombination in cis-*Ru(NCS)$_2$ Diimine Sensitizers with Aromatic Substituents. *ACS Appl. Mater. Interfaces* **2019**, *11* (46), 43223-43234.





ACS Appl. Mater. Interfaces 2017, 9, 39, 33446-33454

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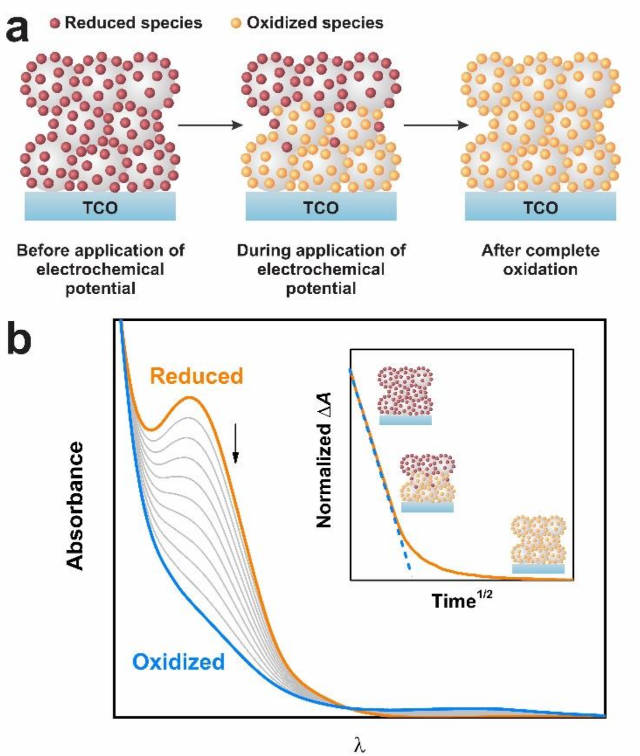

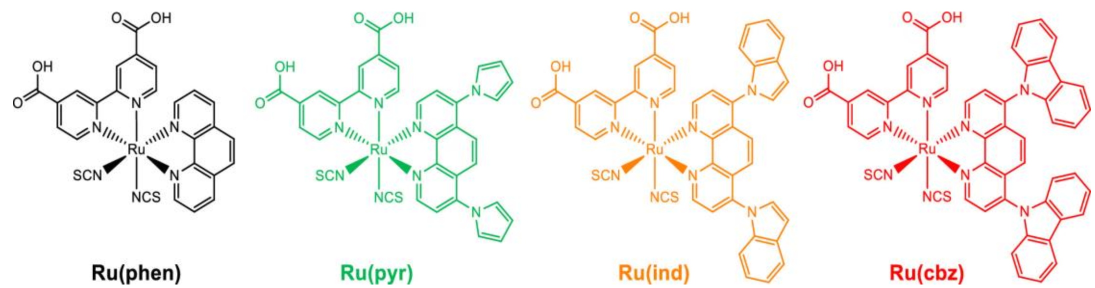

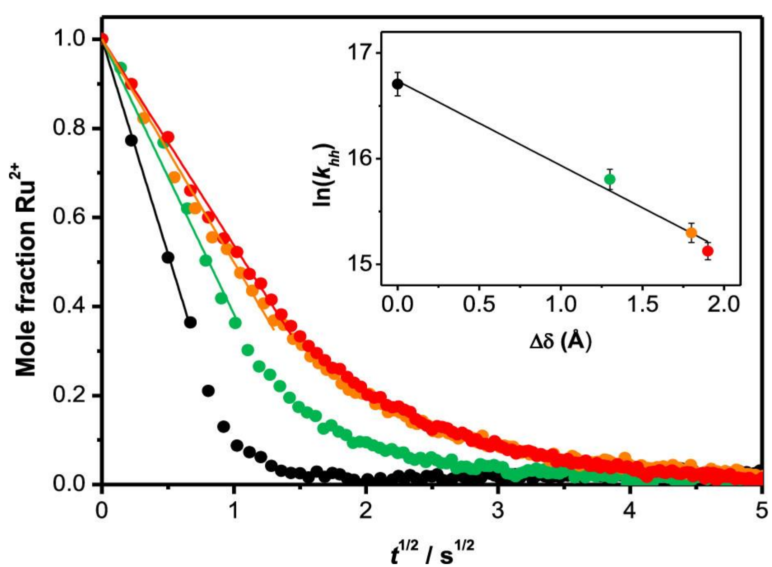

Estudo de caso

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compound	$D_{app}/10^{-8}$ cm^2 s^{-1}	$k_{hh}/10^6$ s^{-1}	H_{DA}/meV	η/%
Ru(phen)	5.1 ± 0.5	14 ± 2	3.8	5.4 ± 0.4
Ru(pyr)	2.5 ± 0.2	5.7 ± 0.7	2.4	3.5 ± 0.3
Ru(ind)	2.1 ± 0.2	4.4 ± 0.4	2.1	4.2 ± 0.4
Ru(cbz)	1.7 ± 0.1	3.7 ± 0.3	1.9	6.1 ± 0.2