Química Orgânica Avançada
Módulo I

Prof. Pierre Mothé Esteves
pesteves@iq.ufrj.br
2562-7444
Labs 622/629A

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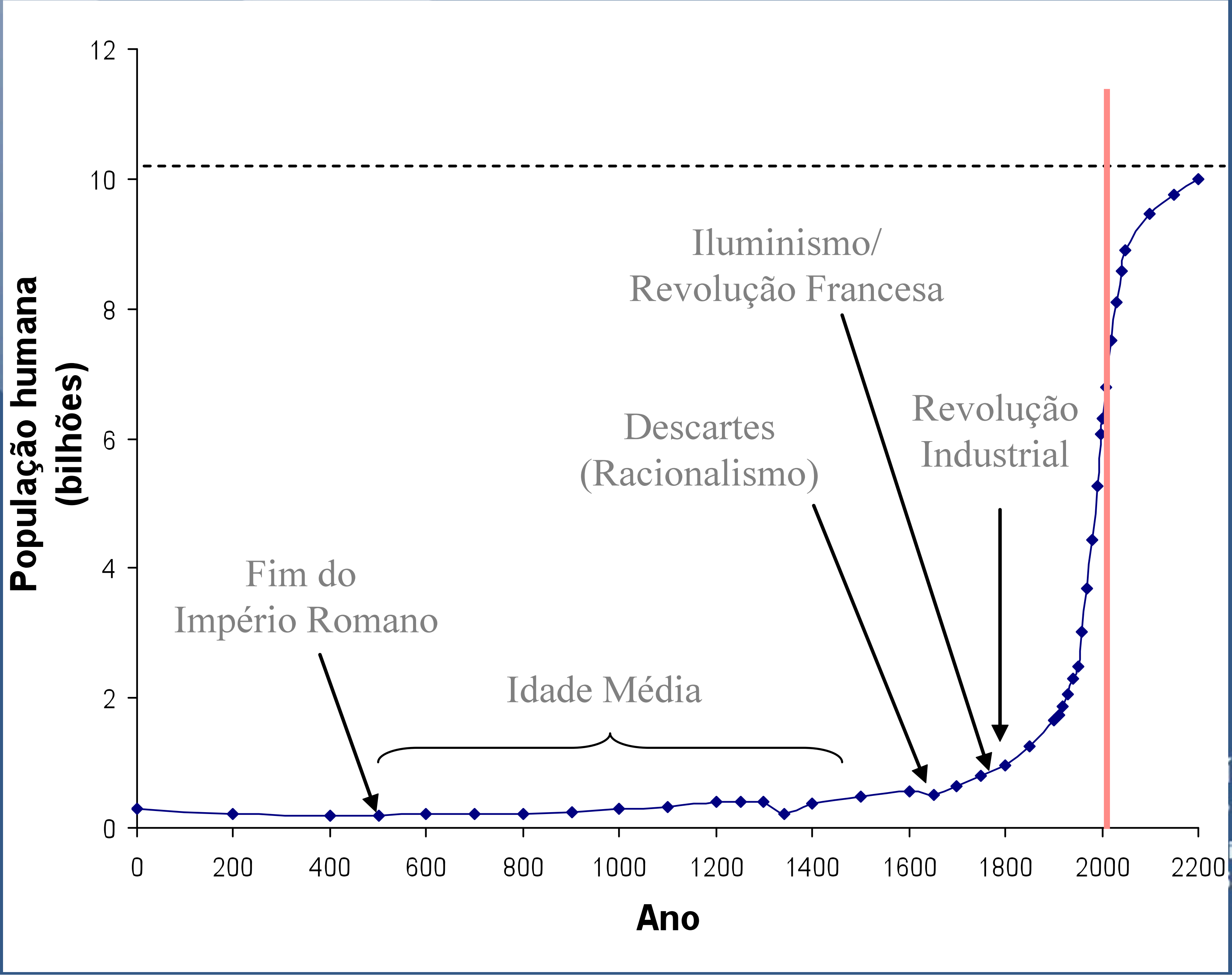
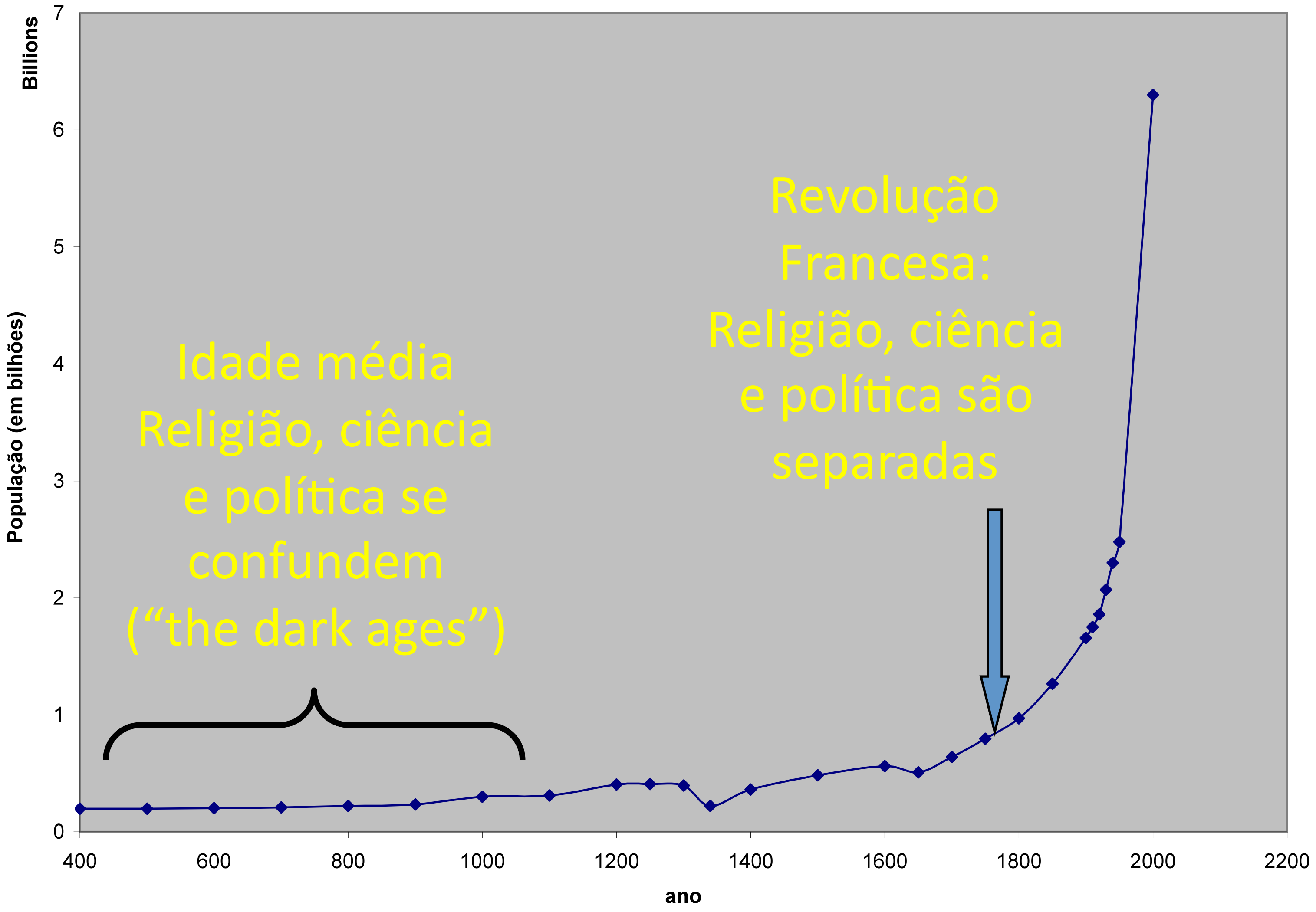
Universidade Federal do Rio de Janeiro
www.iq.ufrj.br
Tel:. 2562-7001 2562-7002

Crescimento Populacional (Dados da ONU)



Ode à razão e à lógica



Idade média
Religião, ciência
e política se
confundem
(“the dark ages”)

Revolução
Francesa:
Religião, ciência
e política são
separadas

ica
aneiro
frj.br
7002

No quê trabalhar

- Olhar o passado ajuda a enxergar o futuro
- O que será importante em 2050?
  - População humana estimada: ~ 10 bilhões de pessoas
  - Rio de Janeiro:
    - Hoje: 6 milhões (1 em cada 5 mora em “comunidades”)
    - 2020: 13 milhões (1 em cada 3 mora em “comunidades”)
    - 2050: 23 milhões ? (1 em cada 1 mora em “comunidades”?)
  - Eu terei 78 anos em 2050,
  - E vocês?

O que vai faltar?

- Água (petróleo do futuro)
- Energia = Conforto
- Saúde
- Planejamento urbano

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Onde está a Química?

- Água (petróleo do futuro)
- Energia = Conforto
- Saúde
- Planejamento urbano
- Etc

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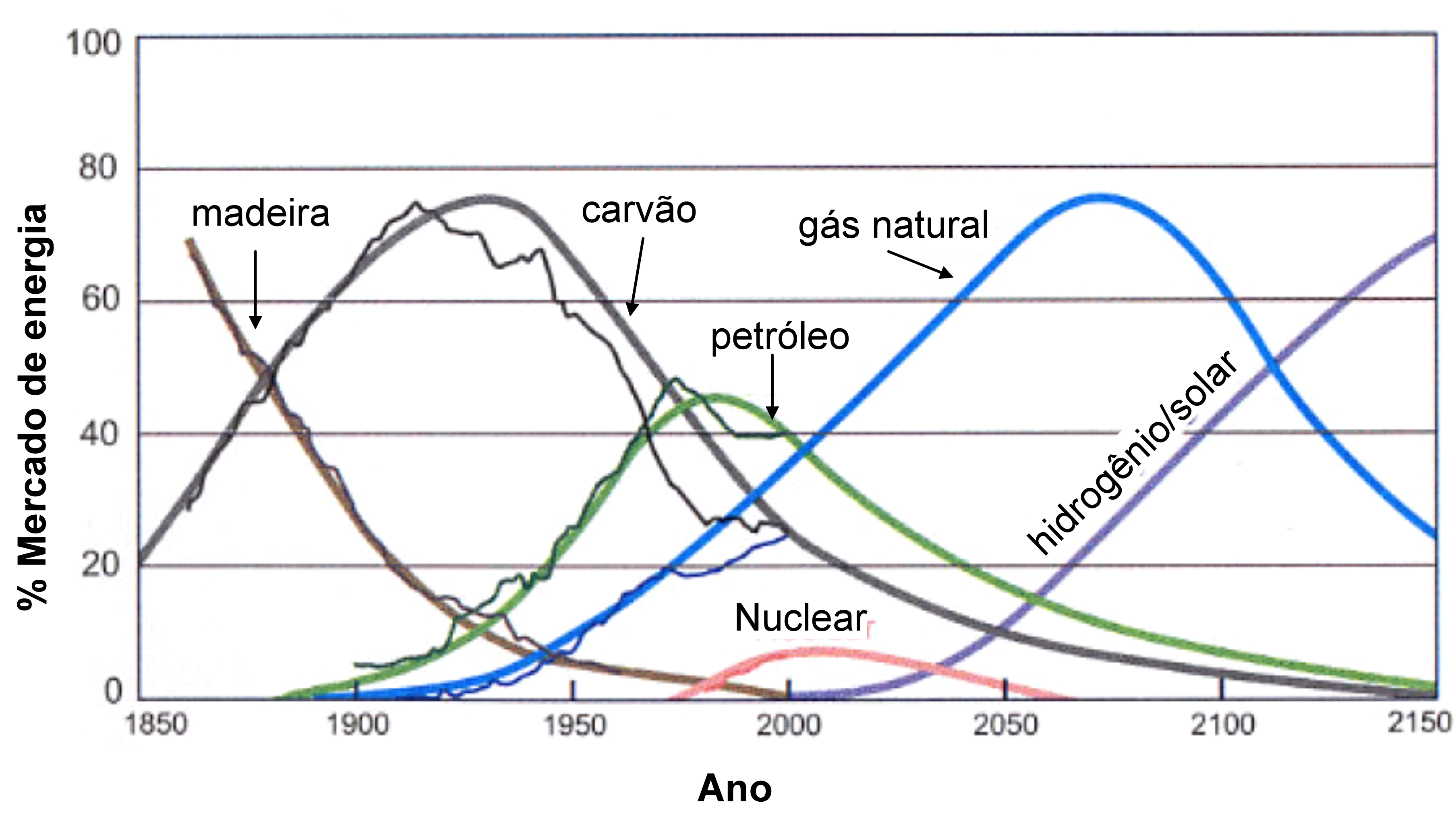
Projeções para o uso de algumas formas de energia no futuro.



Exemplo Química do século XIX

- Derivatização

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Química século XX

- Descoberta do elétron (1898) e sua utilização na Química (Lewis, 1916)
- Mecânica Quântica (1926)
- RMN (Rabi, 1938; Bloch & Purcell 1946)
- Massas (Thomson, Dempster, Aston 1897-1919)
- IV
- UV-Vis
- Cinética → Mecanismos → Novas reações

Qual será a Química do século XXI?

- Mais do mesmo
- Novas ferramentas, que vêem mundo atômico com muito mais detalhe permitirão a descoberta de novos fenômenos e a elucidação de problemas moleculares
- Eletrônica molecular
- Química além da molécula (supramolecular)
  - Nanociência/nanotecnologia
  - Bioquímica
  - Tratamento com células tronco substituirão os fármacos?

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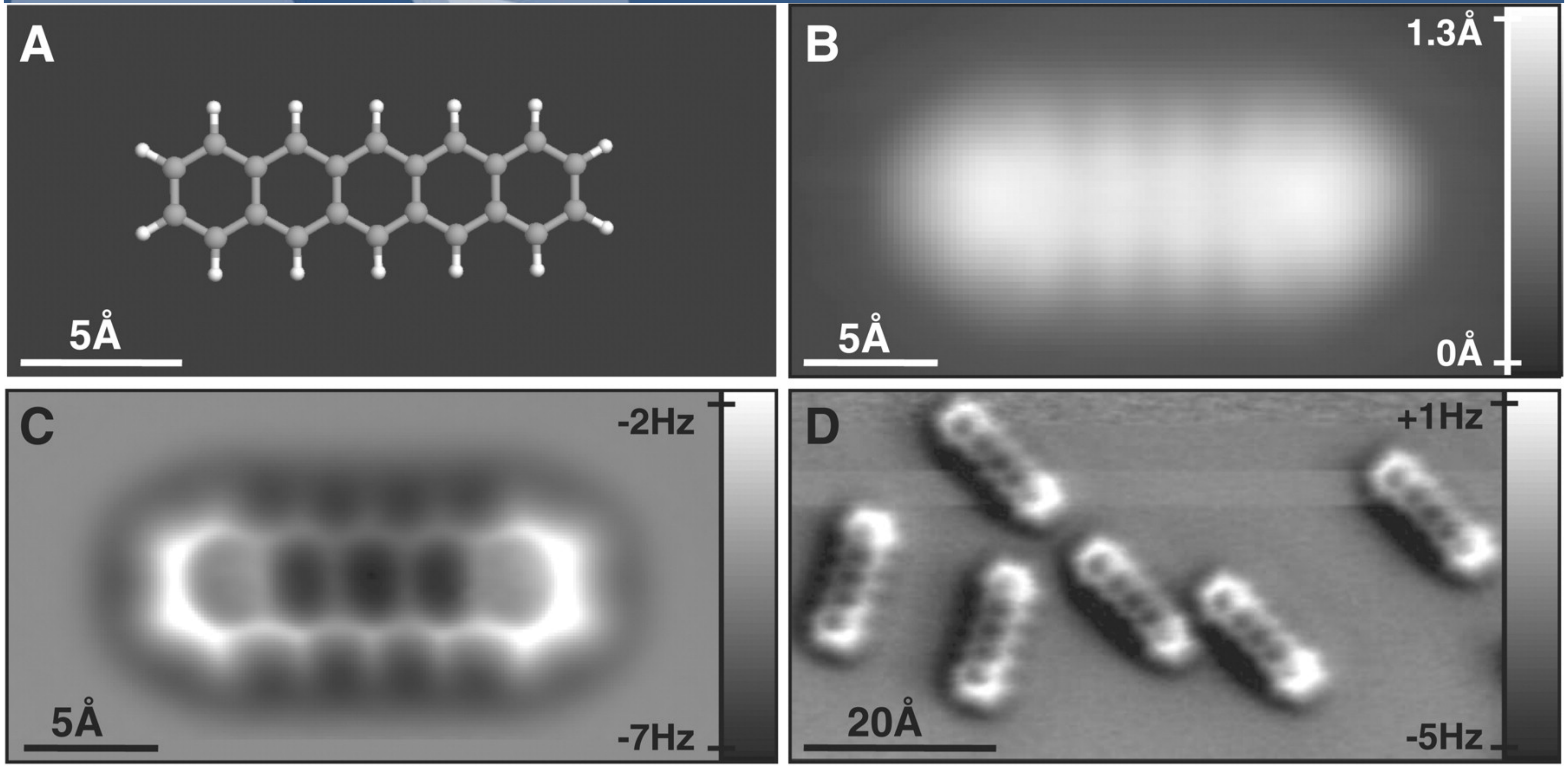
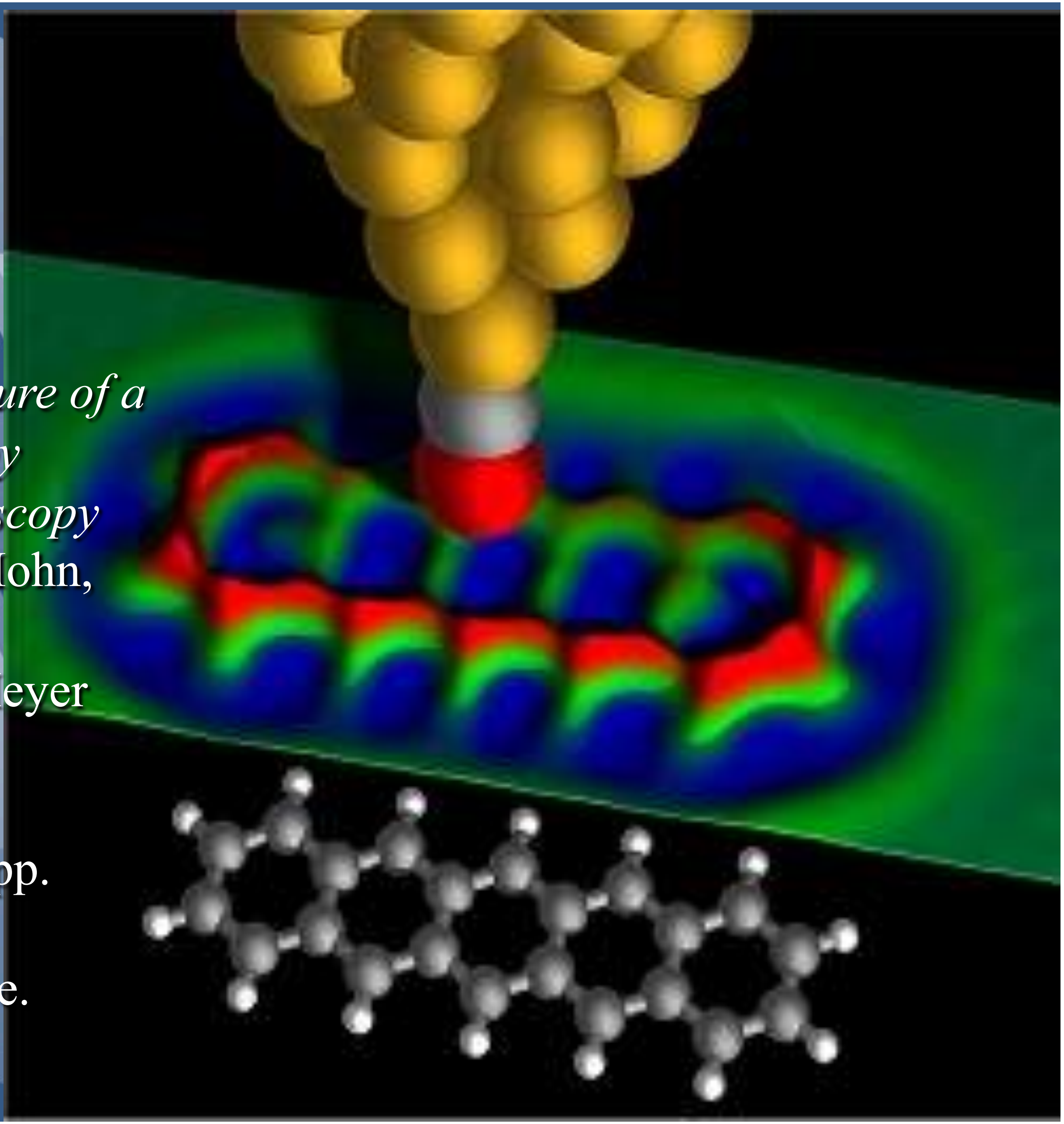
Atualidades: Do que somos capazes?
Primeira “foto” de uma molécula (2009)

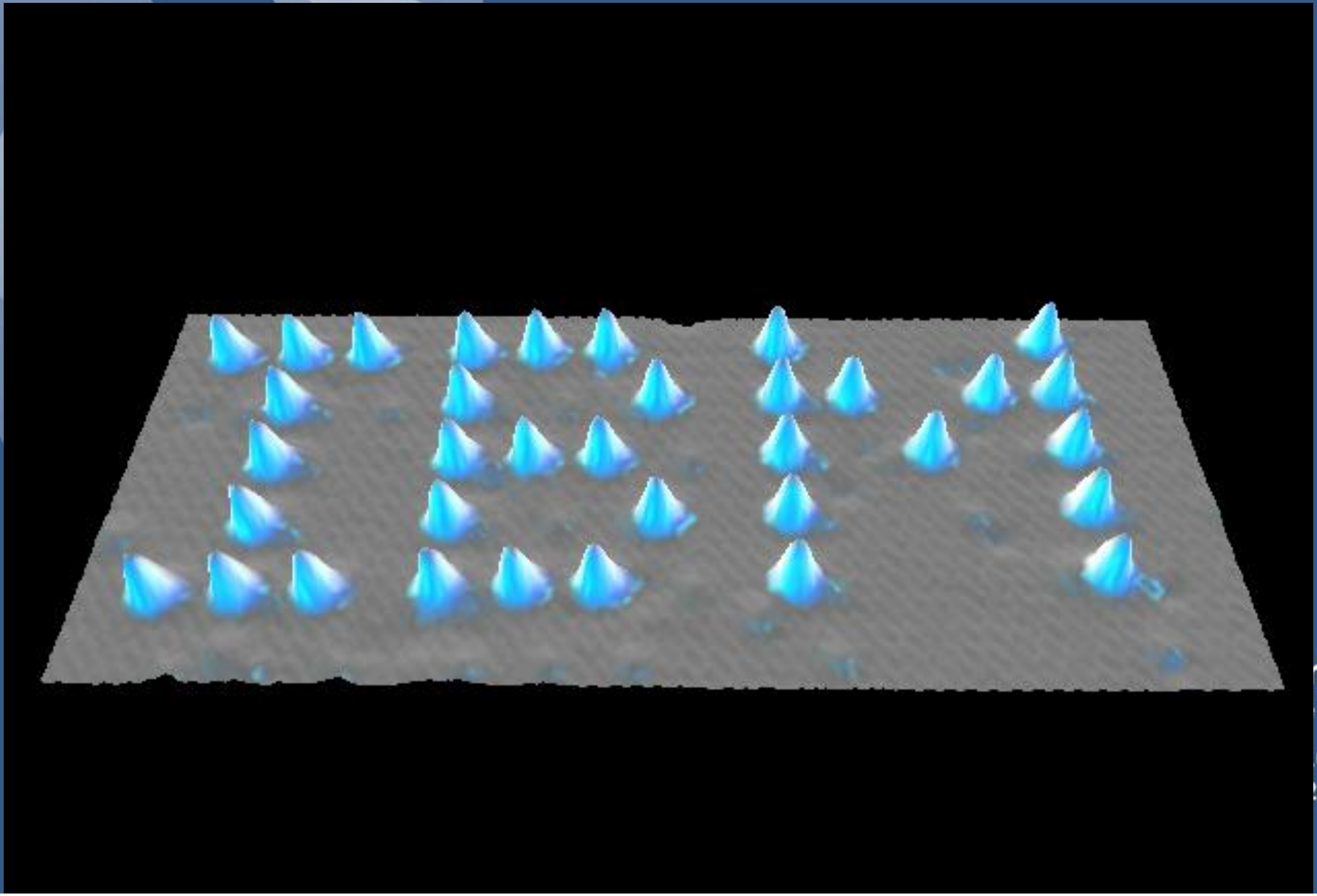


STM and AFM imaging of pentacene on Cu(111). (A) Ball-and-stick model of the pentacene molecule. (B) Constant-current STM and (C and D) constant-height AFM images of pentacene acquired with a CO-modified tip. Imaging parameters are as follows: (B) set point $I = 110$ pA, $V = 170$ mV; (C) tip height $z = -0.1$ Å [with respect to

The Chemical Structure of a
Molecule Resolved by
Atomic Force Microscopy
Leo Gross, Fabian Mohn,
Nikolaj Moll, Peter
Liljeroth, Gerhard Meyer
Science
28 August 2009
Vol.: 325. no. 5944, pp.
1110 - 1114
DOI: 10.1126/science.
1176210



Manipulando átomos



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Janeiro

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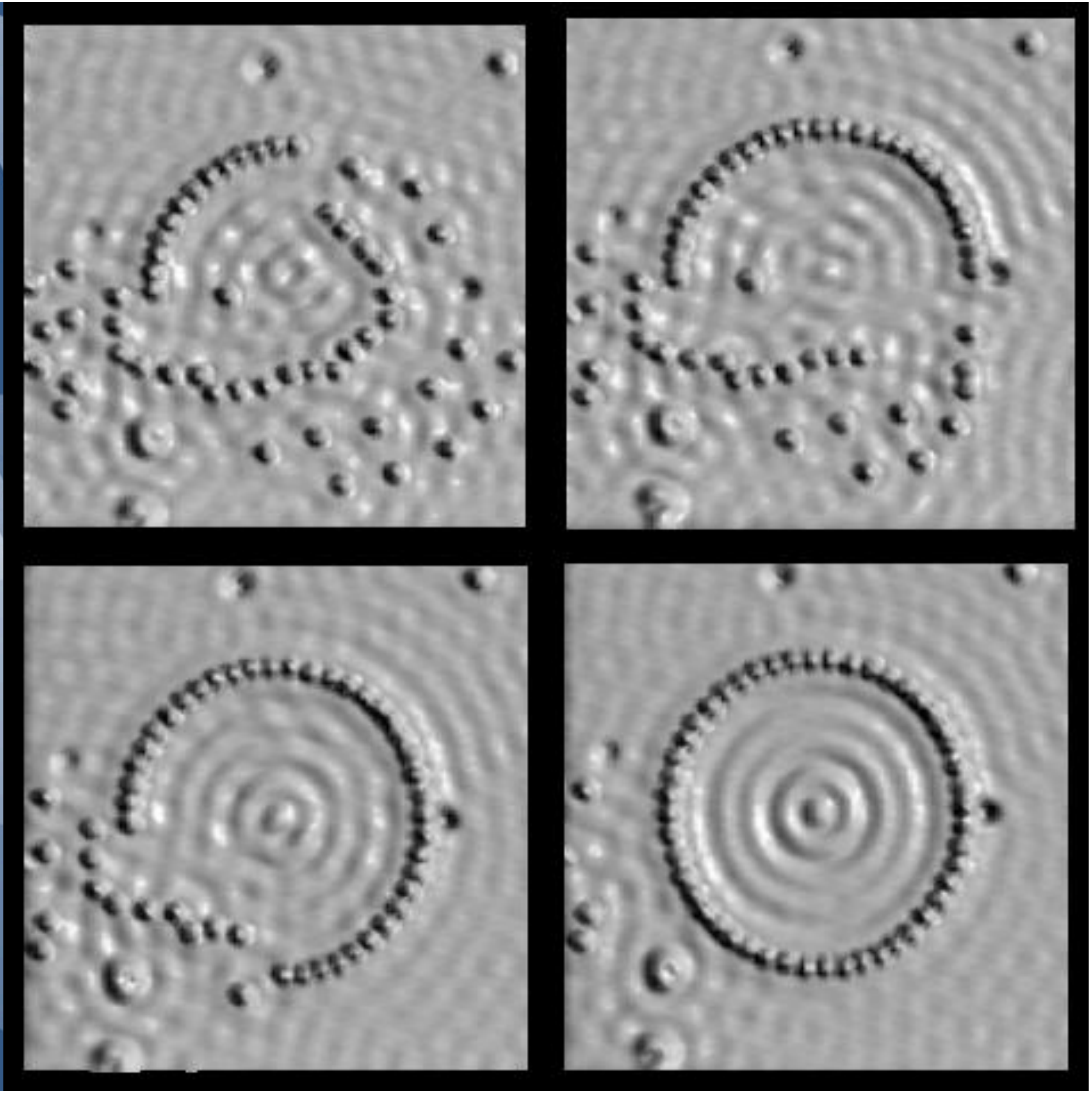
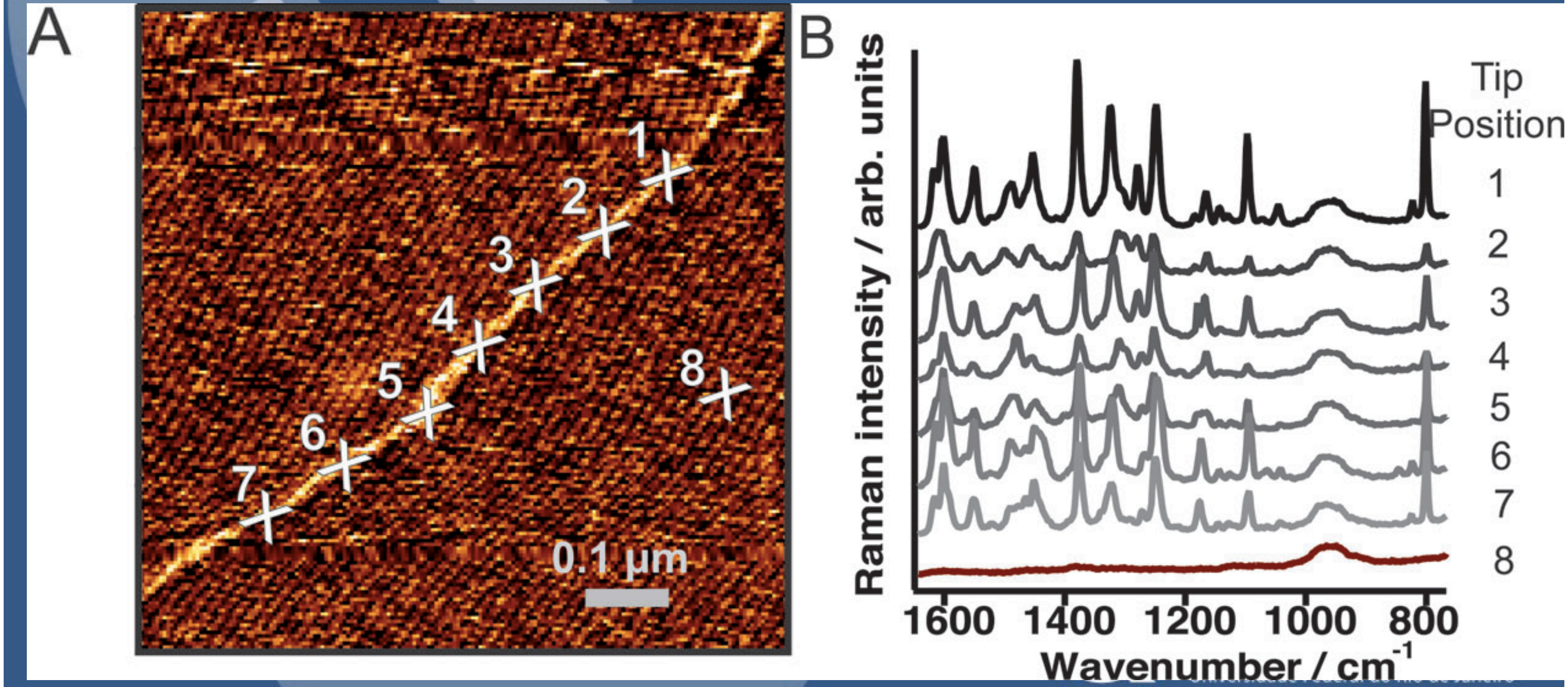
Curral Quântico



Tip Enhanced Raman Spectroscopy (TERS) em uma fita de DNA



E. Bailo and V. Deckert, Angew. Chem., Int. Ed., 2008, 47, 1658.
DOI: 10.1039/b705967c

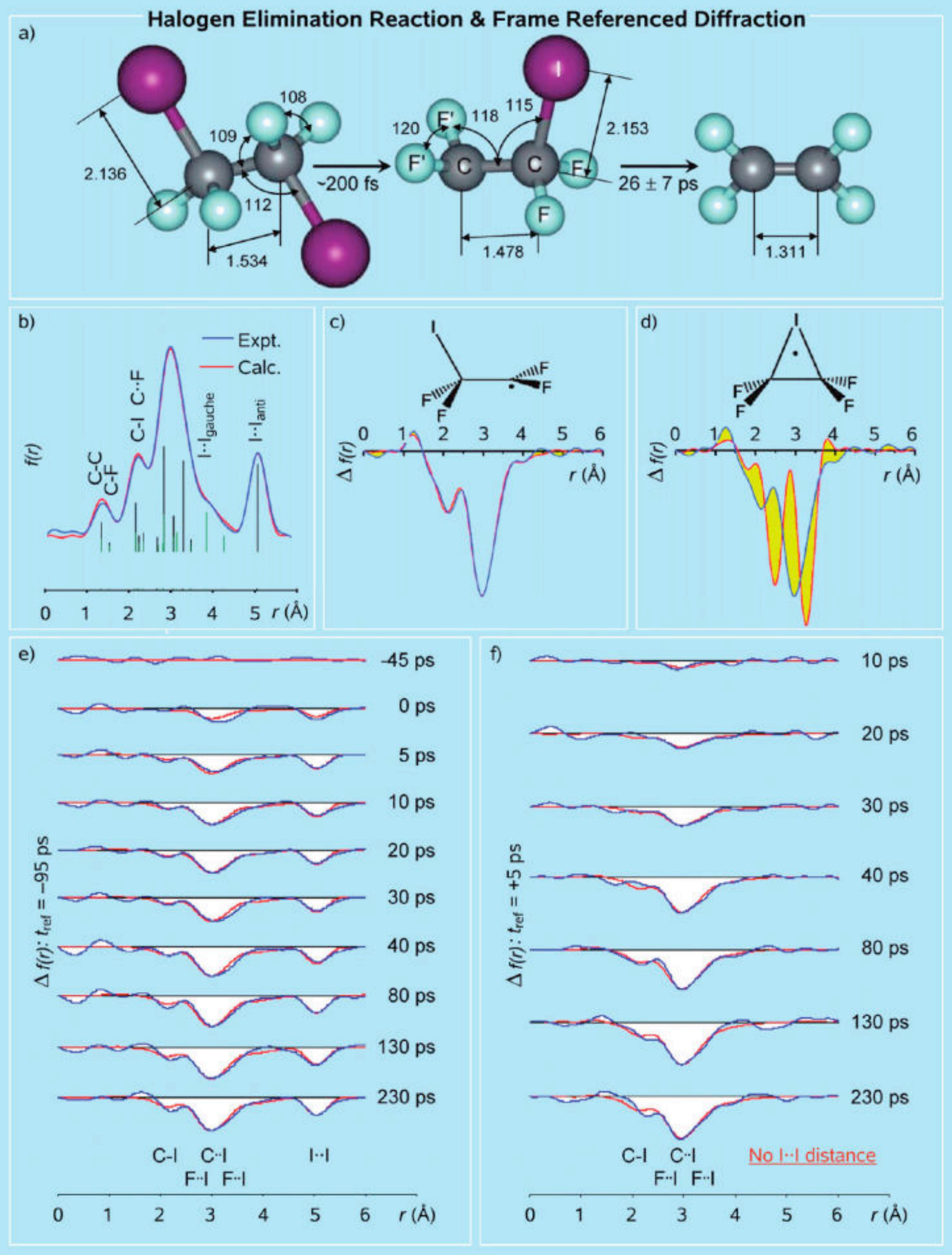
Femtoquímica

- Ver trabalhos de Ahmed Zewail
    - http://www.its.caltech.edu/~femto/
- Espectroscopia de estados de transição

TEM 4D

- Imagem em escala atômica com resolução temporal
- “Filme” molecular

J. Am. Chem. Soc., 2009, 131 (50), pp 17998–18015
DOI: 10.1021/ja907432p



Novas ferramentas

- Ampliação das antigas ferramentas (RMN, MS, IV, química computacional, etc)
- Novas ferramentas
  - Microscopia
    - com resolução atômica: STM, AFM, SEM, TEM
    - TERS, SERS
    - Raman Confocal
    - com resolução atômica e temporal:
      - ultrafast electron diffraction (UED),
      - ultrafast electron crystallography (UEC),
      - ultrafast electron microscopy (UEM)

Twenty-first century chemistry represents the forefront of the molecular sciences. New theories, concepts, and ideas facilitated by advances in analytical techniques and instrumentation revolutionized the practice of chemistry in the latter part of the 20th century. Advances in NMR spectroscopy, mass spectrometry, synchrotron and X-ray techniques, single-molecule spectroscopy, microscopy, computations, lasers, and others, along with tremendous strides in synthesis and coupled with tools of biology such as genetic engineering, allow us to examine complex chemical and biological phenomena, unimagined just a few decades ago, at the molecular, atomic, and even subatomic levels.

Peter J. Stang
J. Am. Chem. Soc., 2009, 131 (35), p 12496
DOI: 10.1021/ja903812n

Algumas coisas não mudam

- Criatividade é a mais valorizadas das habilidades humanas
- Estar em dia com a literatura (estudo contínuado) é a uma das chaves do sucesso
  - Tipos de literatura
    - Notas
    - Comunicações
    - Artigos
    - Revisões
    - Livros
    - Pespectivas

Algumas coisas não mudam

- Trabalho duro e sério

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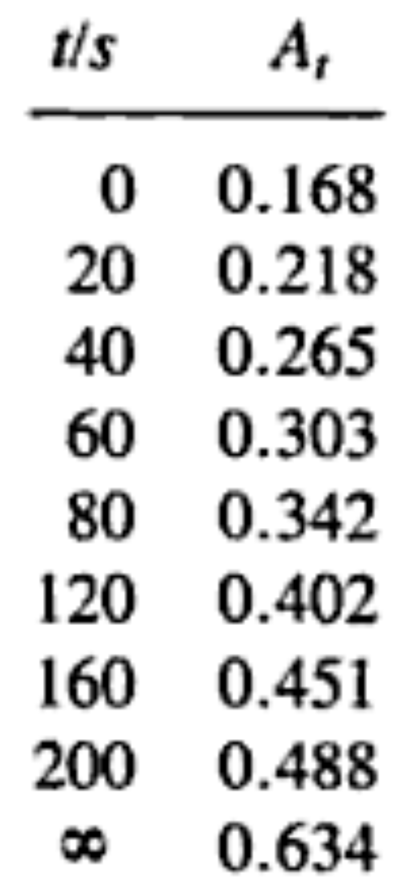
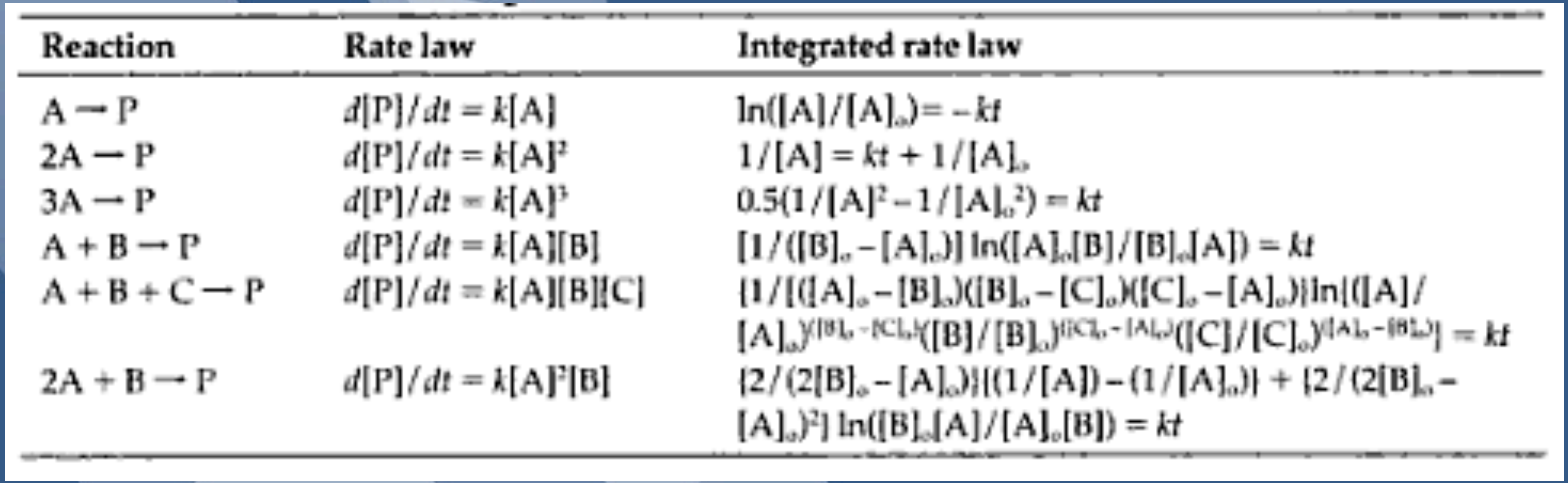
Exercício: Absorvância x tempo para hidrólise de benzoato de p-nitrofenila

- Concentração inicial éster: 8 x 10-6 mol/L
- Força iônica = 0.2 M
- 25.0 ºC
- Medidas a 400nm, cubeta 5 cm



t/s	A_t
0	0.168
20	0.218
40	0.265
60	0.303
80	0.342
120	0.402
160	0.451
200	0.488
∞	0.634



Reaction	Rate law	Integrated rate law
$A \rightarrow P$	$d[P]/dt = k[A]$	$\ln([A]/[A]_o) = -kt$
$2A \rightarrow P$	$d[P]/dt = k[A]^2$	$1/[A] = kt + 1/[A]_o$
$3A \rightarrow P$	$d[P]/dt = k[A]^3$	$0.5(1/[A]^2 - 1/[A]_o^2) = kt$
$A + B \rightarrow P$	$d[P]/dt = k[A][B]$	$[1/([B]_o - [A]_o)] \ln([A]_o[B]/[B]_o[A]) = kt$
$A + B + C \rightarrow P$	$d[P]/dt = k[A][B][C]$	$\{1/[([A]_o - [B]_o)([B]_o - [C]_o)([C]_o - [A]_o)]\} \ln\{([A]/[A]_o)^{([B]_o - [C]_o)}([B]/[B]_o)^{([C]_o - [A]_o)}([C]/[C]_o)^{([A]_o - [B]_o)}\} = kt$
$2A + B \rightarrow P$	$d[P]/dt = k[A]^2[B]$	$\{2/(2[B]_o - [A]_o)\}\{(1/[A]) - (1/[A]_o)\} + \{2/(2[B]_o - [A]_o)^2\} \ln([B]_o[A]/[A]_o[B]) = kt$

$$\frac{d[\mathrm{P}]}{dt} = k[\mathrm{A}][\mathrm{B}]$$

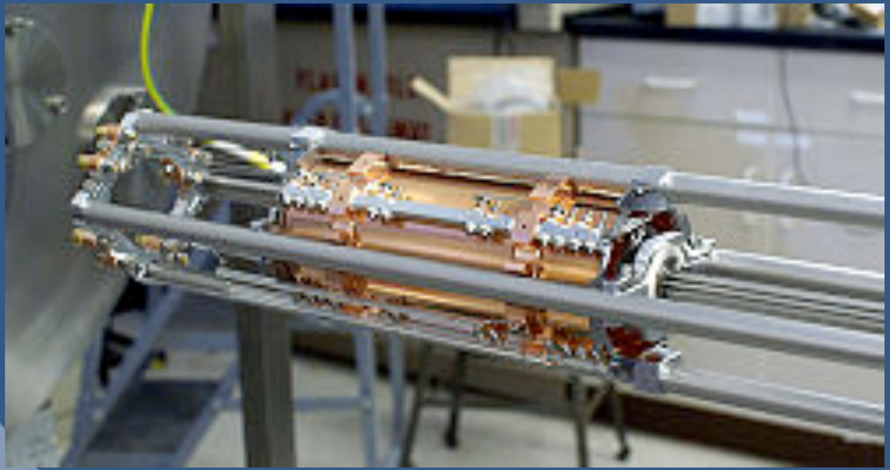
$$\left(\frac{1}{[\mathrm{B}]_o - [\mathrm{A}]_o}\right)\ln\left(\frac{[\mathrm{A}]_o[\mathrm{B}]}{[\mathrm{B}]_o[\mathrm{A}]}\right) = kt$$

$$\mathrm{A} \rightleftharpoons \mathrm{B}$$

$$\frac{d[x]}{dt} = k_f([\mathrm{A}]_o - [x]) - k_r([\mathrm{B}]_o + [x])$$

$$\ln\left(\frac{k_f[\mathrm{A}]_o - k_r[\mathrm{B}]_o}{k_f[\mathrm{A}]_o - k_r[\mathrm{B}]_o - (k_f + k_r)[x]}\right) = (k_f + k_r)t$$

Ion Cyclotron Resonance (FTMS)



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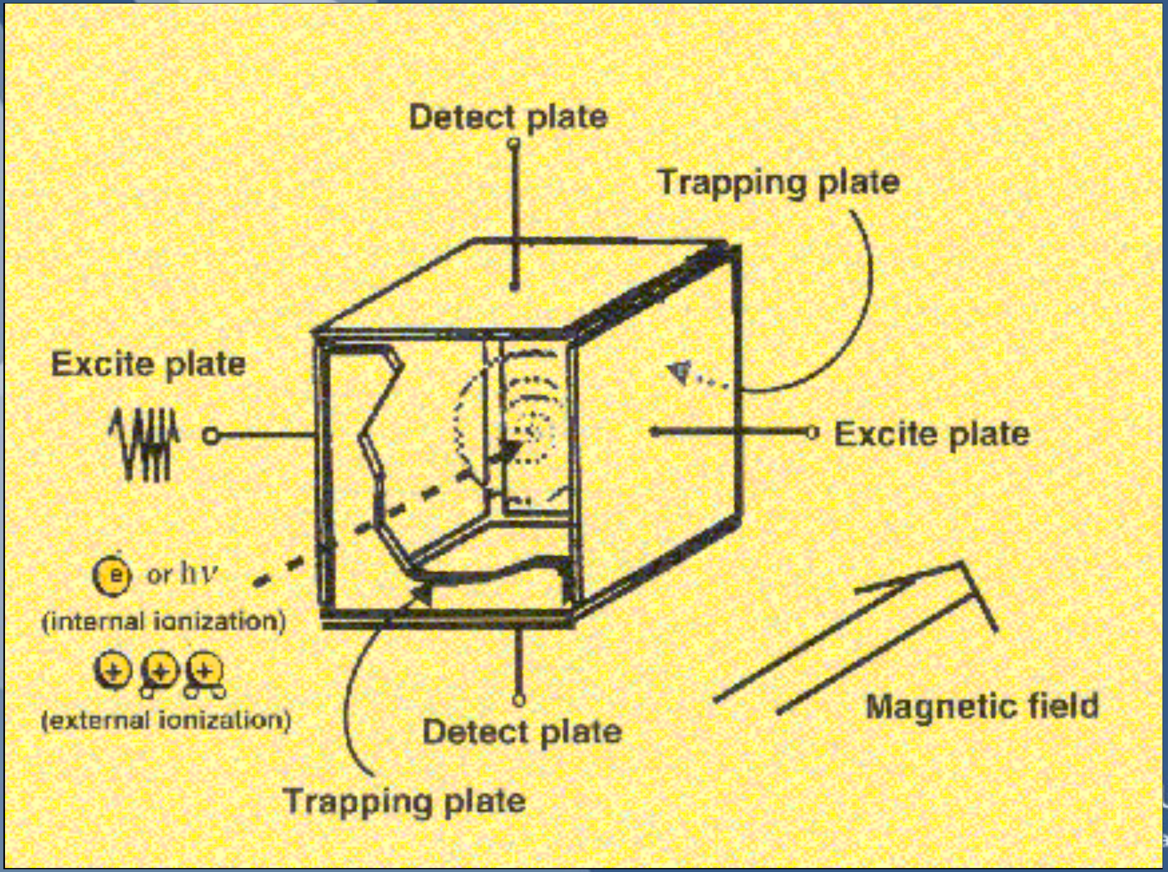
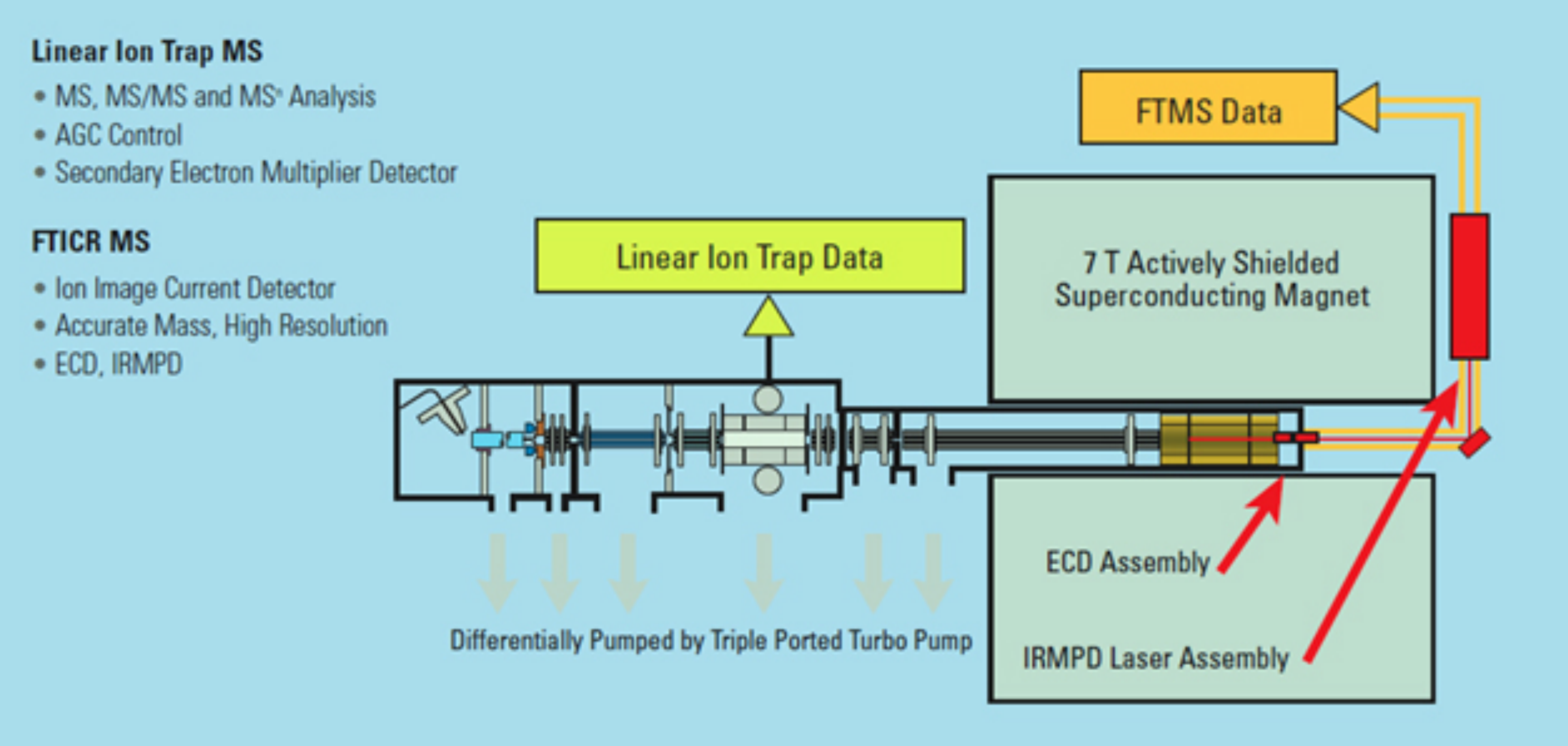
FT-ICR-MS



http://www.asms.org

Funcionamento

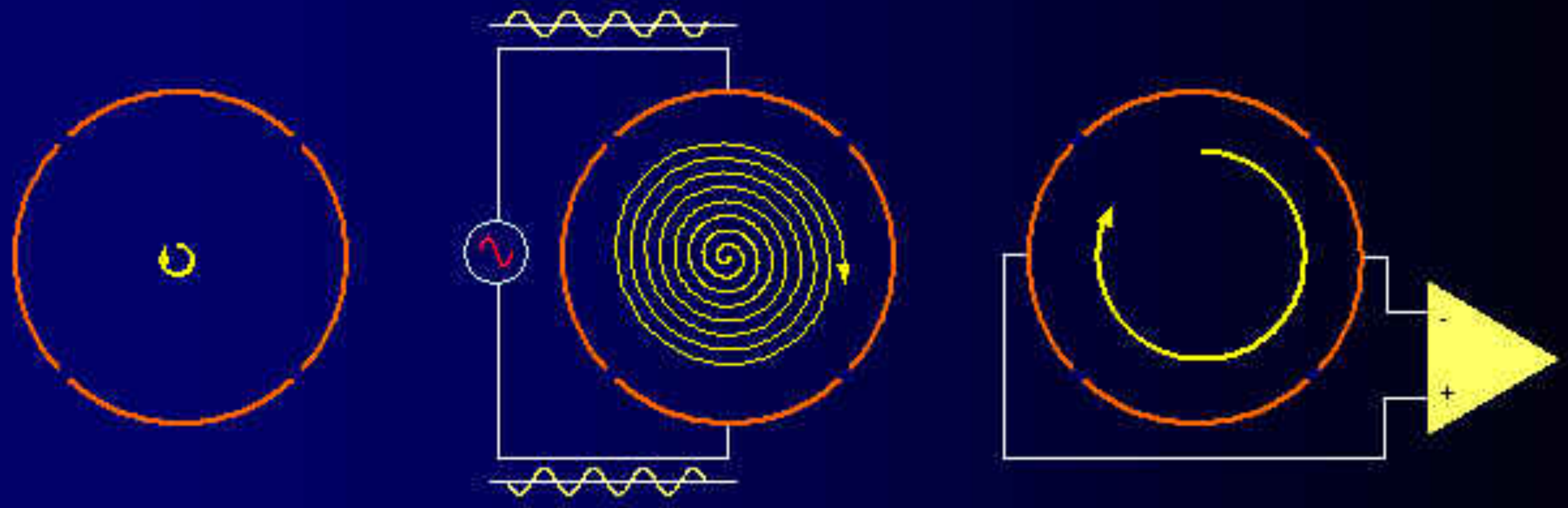


Linear Ion Trap MS

- MS, MS/MS and MS^n Analysis
- AGC Control
- Secondary Electron Multiplier Detector

FTICR MS

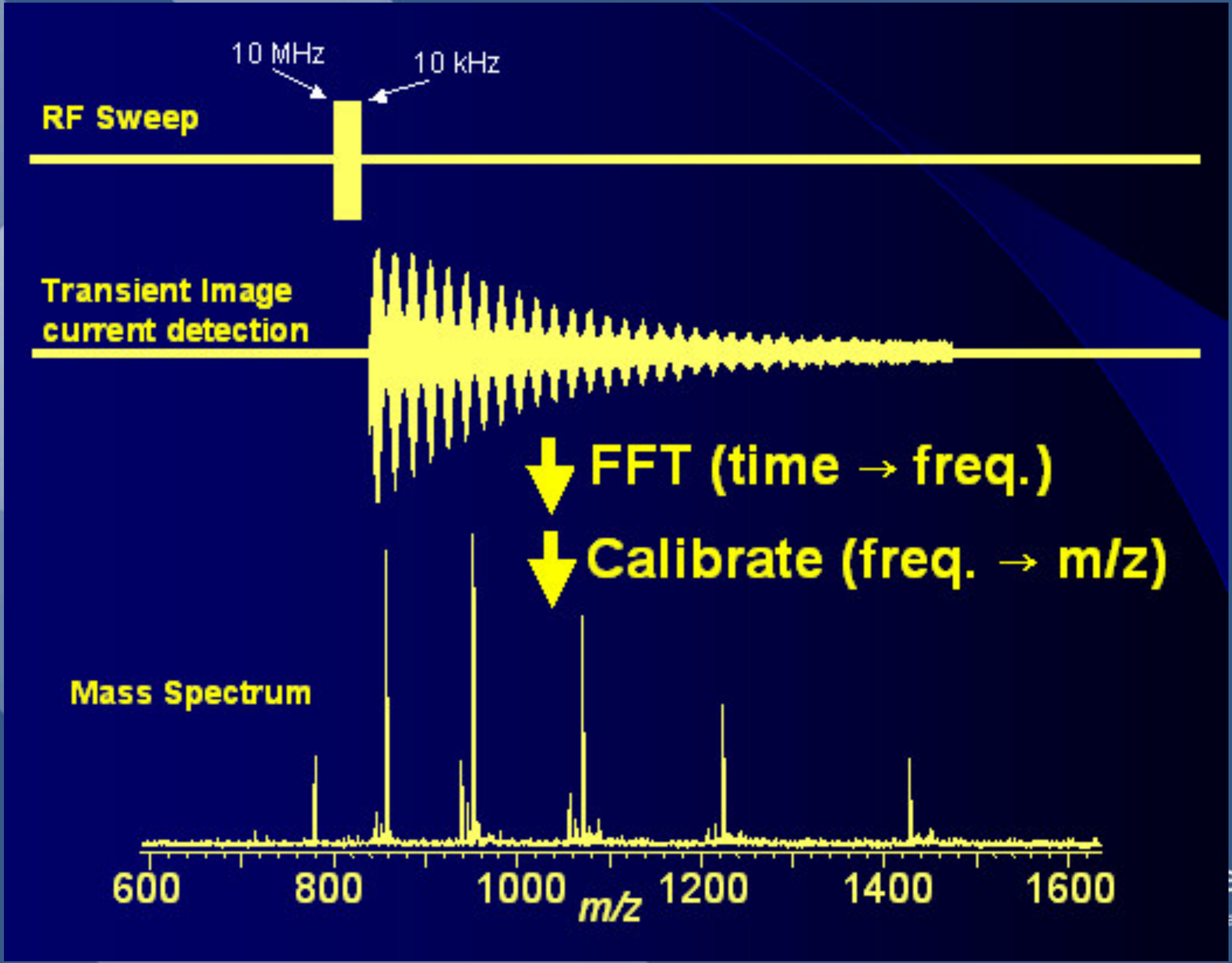
- Ion Image Current Detector
- Accurate Mass, High Resolution
- ECD, IRMPD



Ions are trapped and oscillate with low, incoherent, thermal amplitude

Excitation sweeps resonant ions into a large, coherent cyclotron orbit

Preamplifier and digitizer pick up the induced potentials on the cell.


10 MHz
10 kHz
RF Sweep
Transient Image current detection
FFT (time → freq.)
Calibrate (freq. → m/z)
Mass Spectrum
600
800
1000
m/z
1200
1400
1600

(a) $PhNO_2$ + HO-

(b) $PhNO_2$ + F-

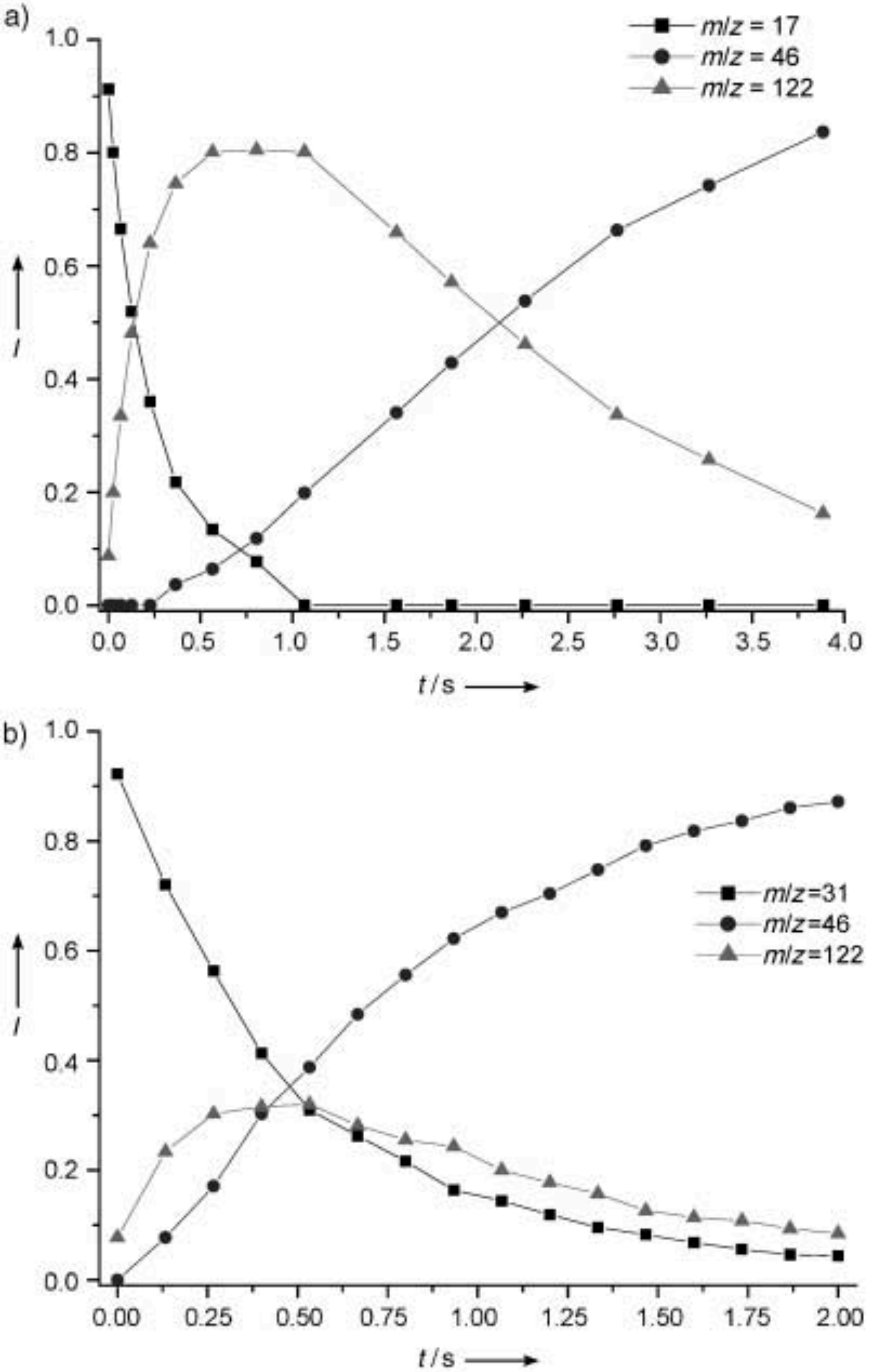
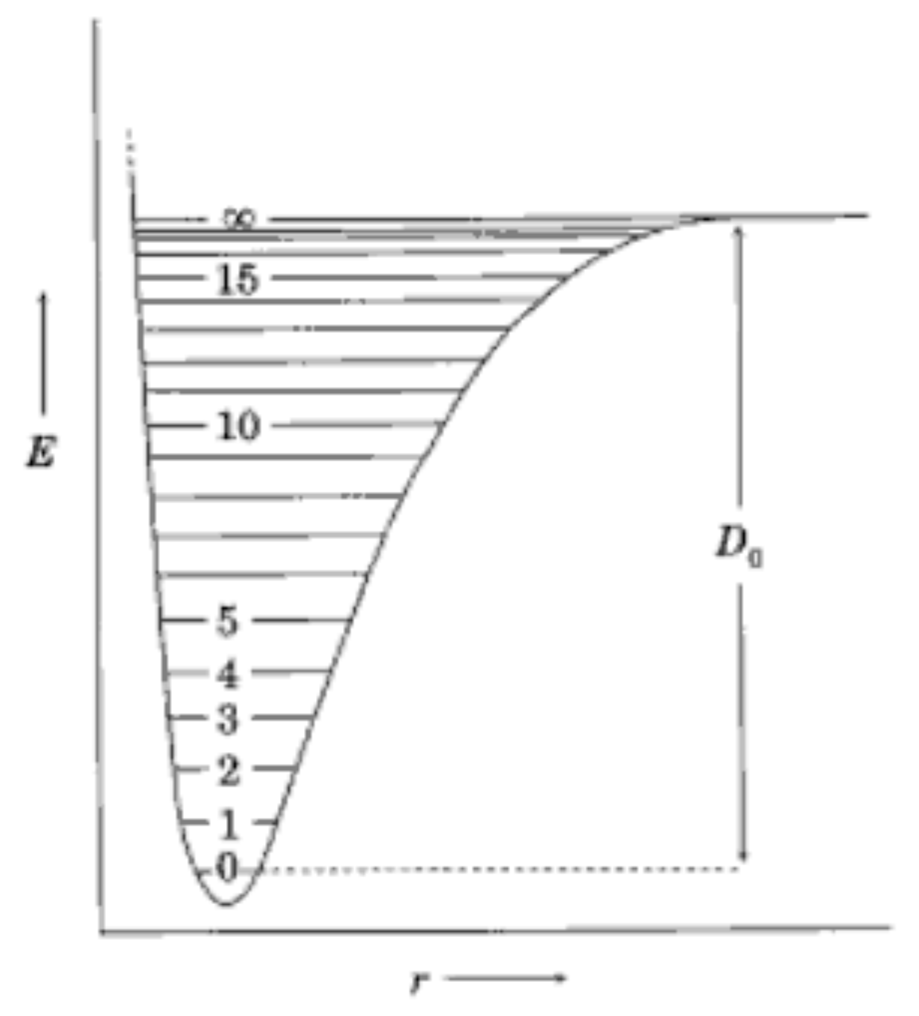


Figure 2. a) Kinetic plot of the gas-phase reaction of OH^- ($m/z=17$) with nitrobenzene reveals rapid proton transfer to yield $C_6H_4NO_2^-$ ($m/z=122$) and H_2O. The subsequent reaction of the $C_6H_4NO_2^-$ ion with neutral H_2O yields NO_2^- ($m/z=46$) and phenol. This secondary reaction is clearly observed from the delay in the appearance of the NO_2^- ion. b) A similar kinetic plot of the gas-phase reaction of MeO^- ($m/z=31$) with nitrobenzene reveals competition between proton transfer (to yield $C_6H_4NO_2^-$ ($m/z=122$) and methanol) and NO_2^- ($m/z=46$) displacement (with formation of anisole). $C_6H_4NO_2^-$ ($m/z=122$) then undergoes a subsequent reaction with neutral H_2O (used to generate MeO^- from the reaction of OH^- with MeOH) to yield NO_2^- ($m/z=46$) and phenol as in Figure 2a.

Angew. Chem. Int. Ed. 2004, 43, 3588 –3590

Efeito de Isótopos na Cinética



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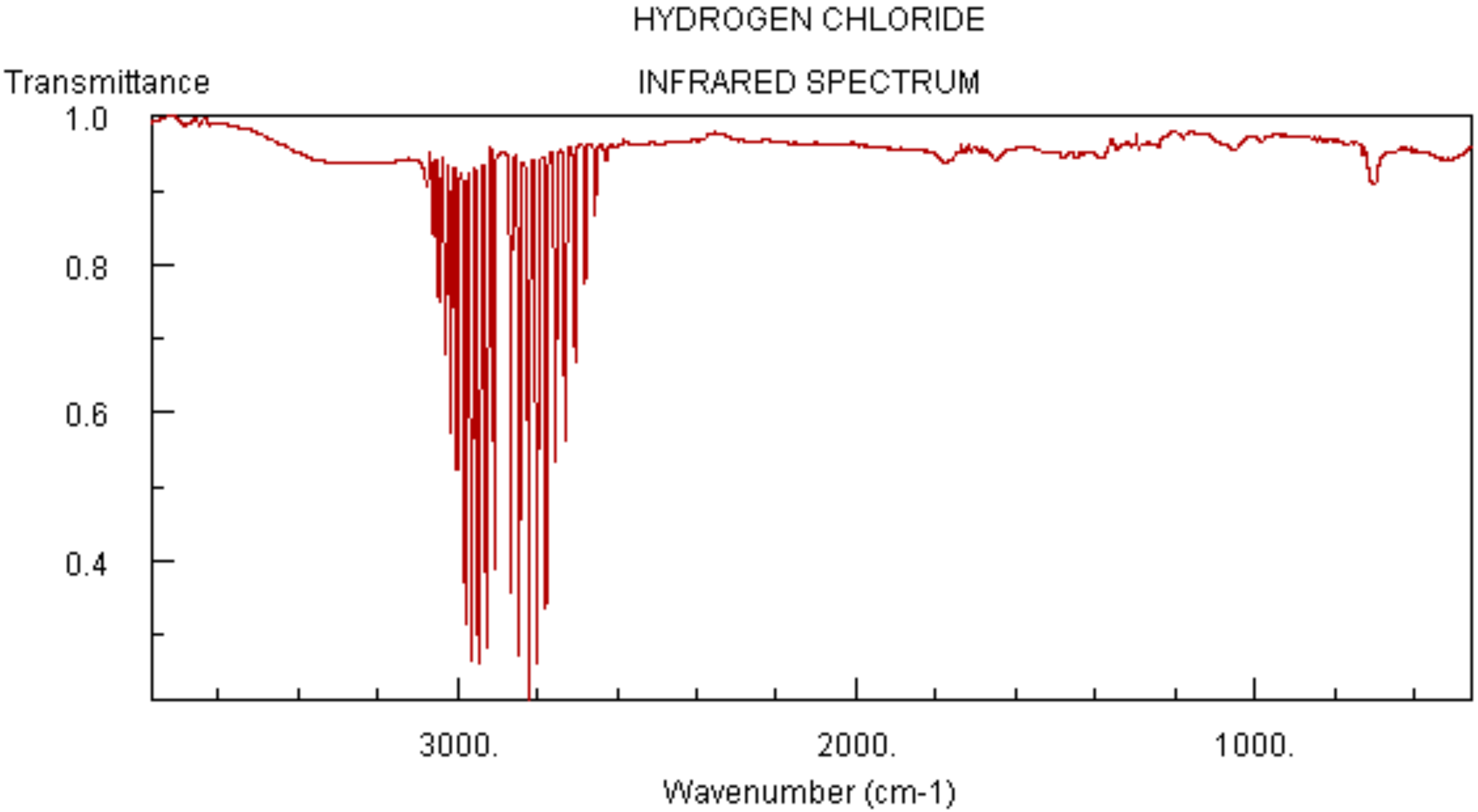
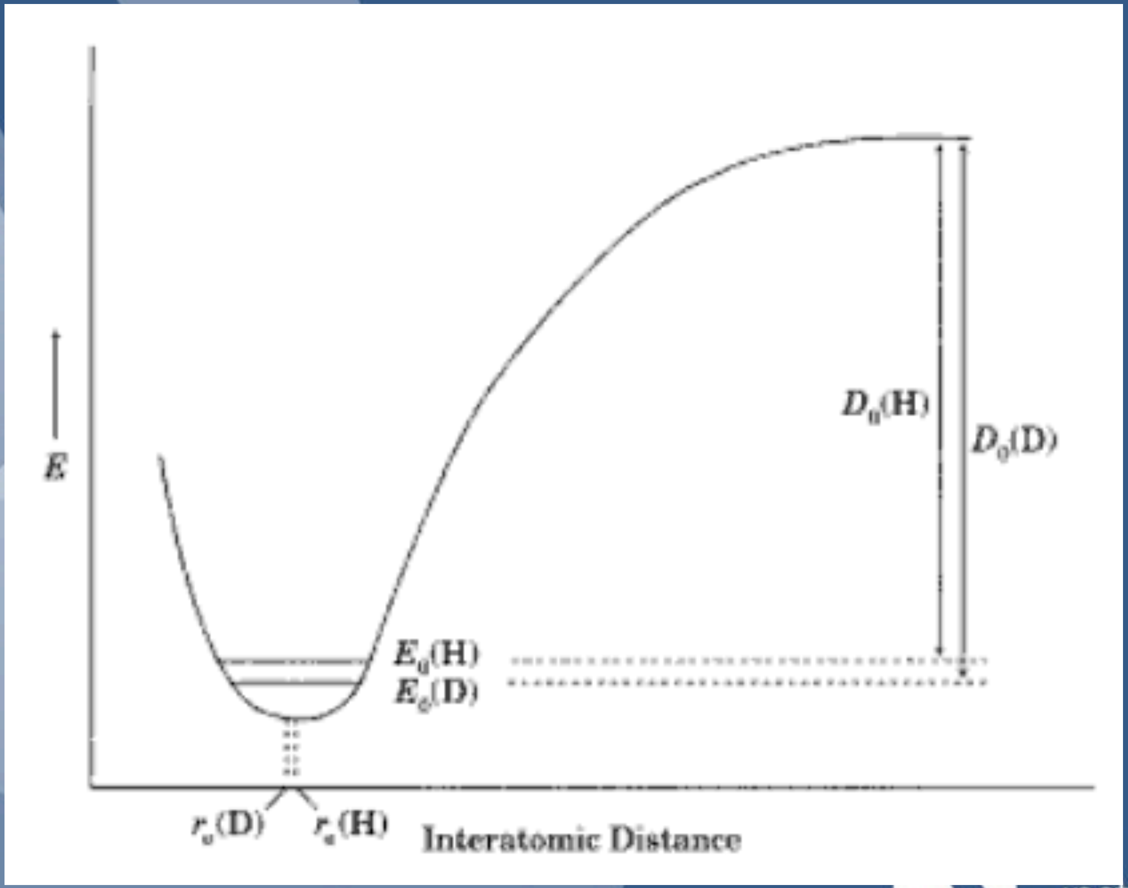
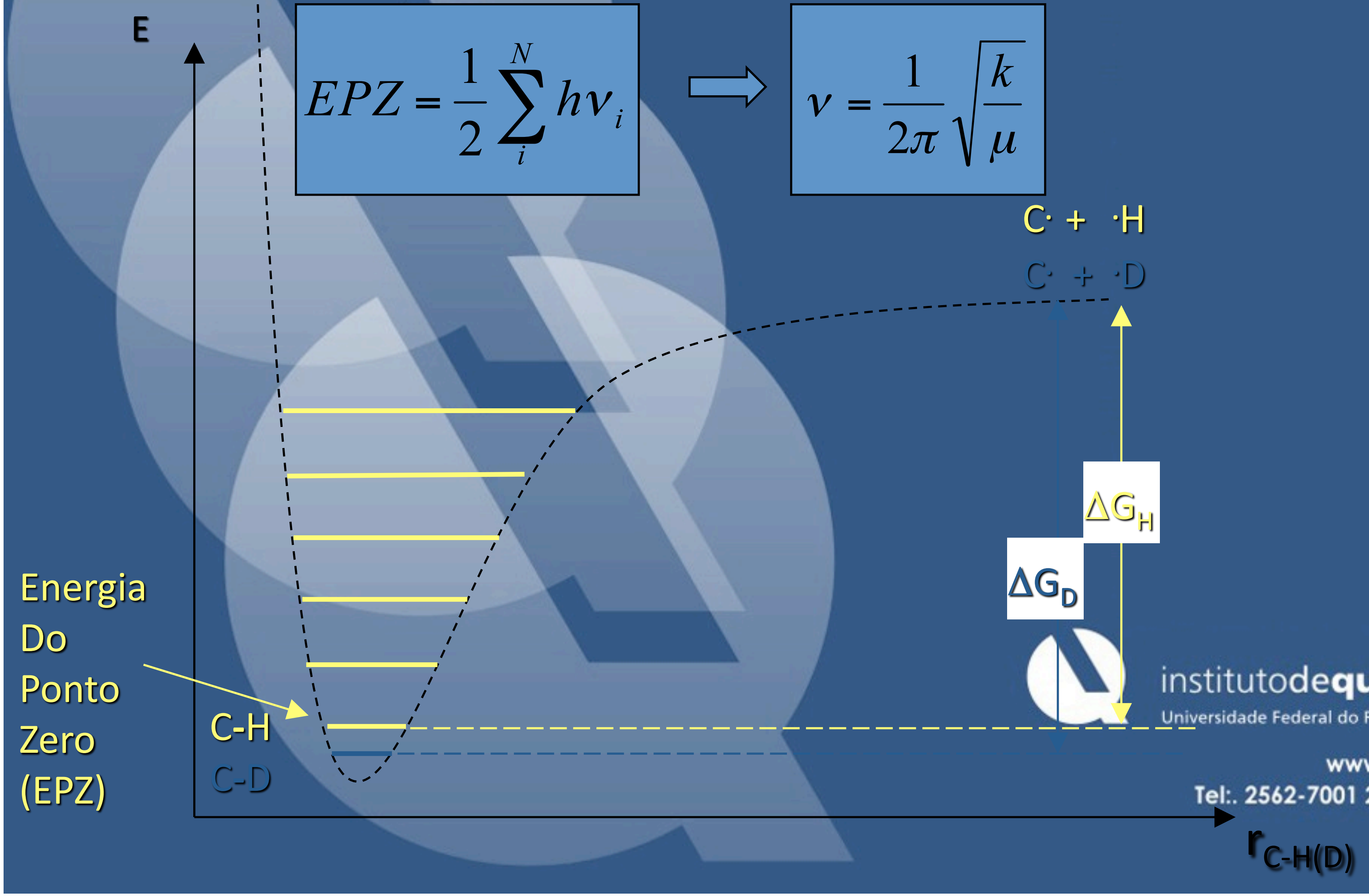

HYDROGEN CHLORIDE
INFRARED SPECTRUM
Transmittance
1.0
0.8
0.6
0.4
3000.
2000.
1000.
Wavenumber (cm-1)

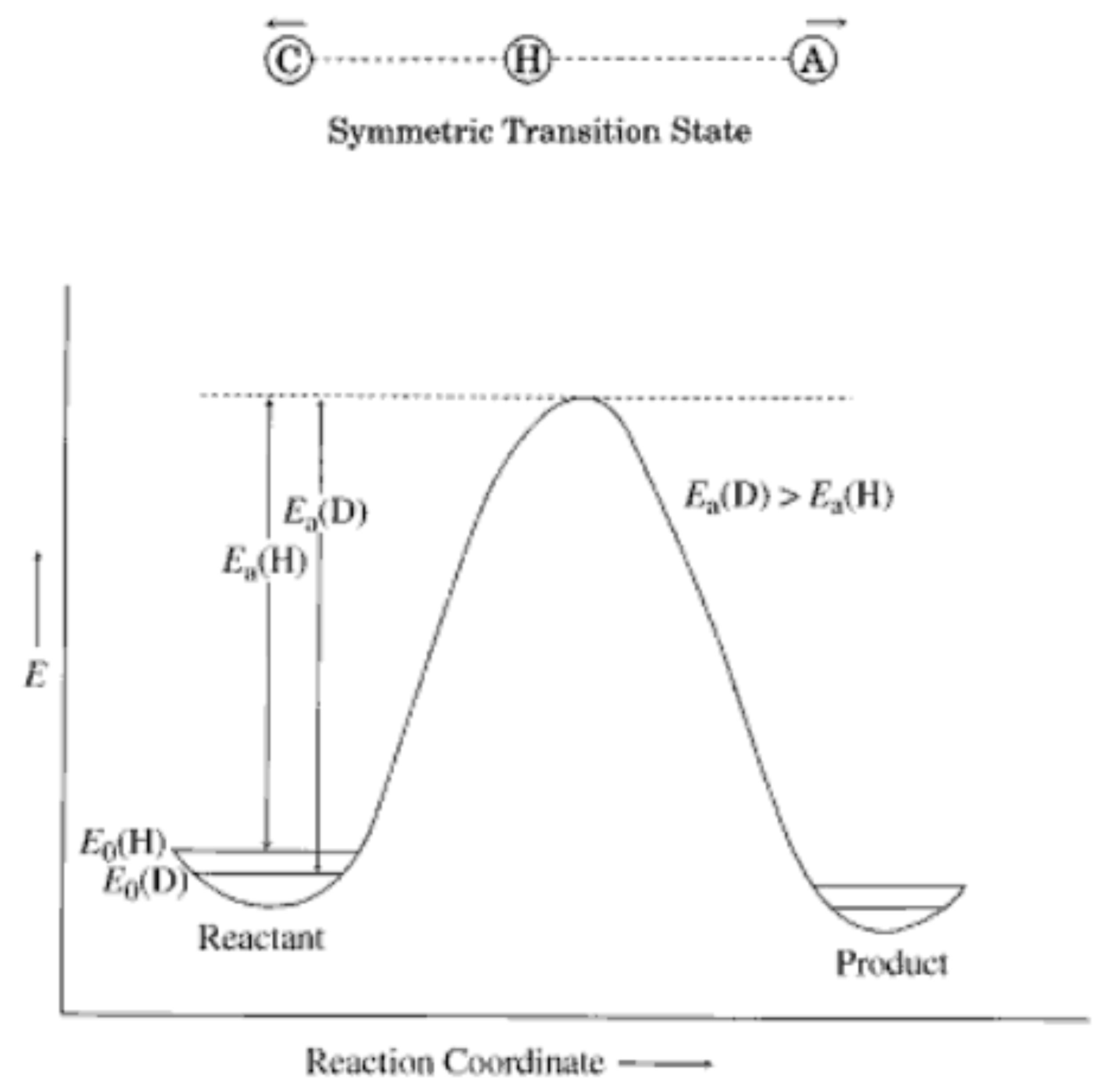

E
D0(H)
D0(D)
E0(H)
E0(D)
re(D)
re(H)
Interatomic Distance

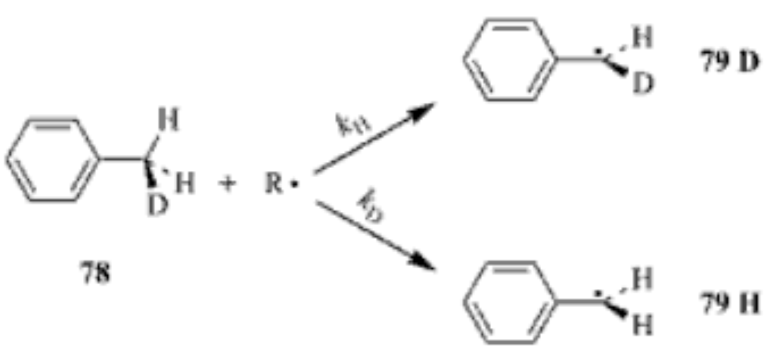
Efeito Cinético Isotópico



$$EPZ = \frac{1}{2}\sum_{i}^{N} h\nu_i \Rightarrow \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Energia
Do
Ponto
Zero
(EPZ)


C
H
A
Symmetric Transition State
$E_a(D)$
$E_a(H)$
$E_a(D) > E_a(H)$
E
$E_0(H)$
$E_0(D)$
Reactant
Product
Reaction Coordinate



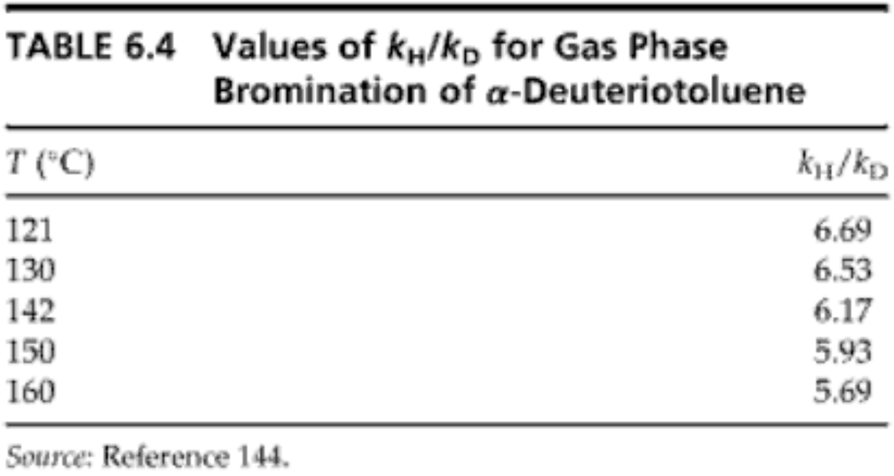
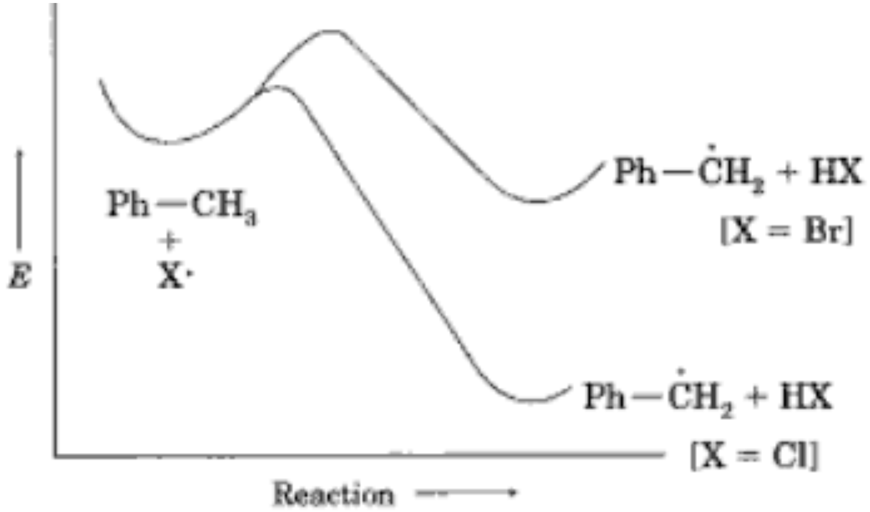
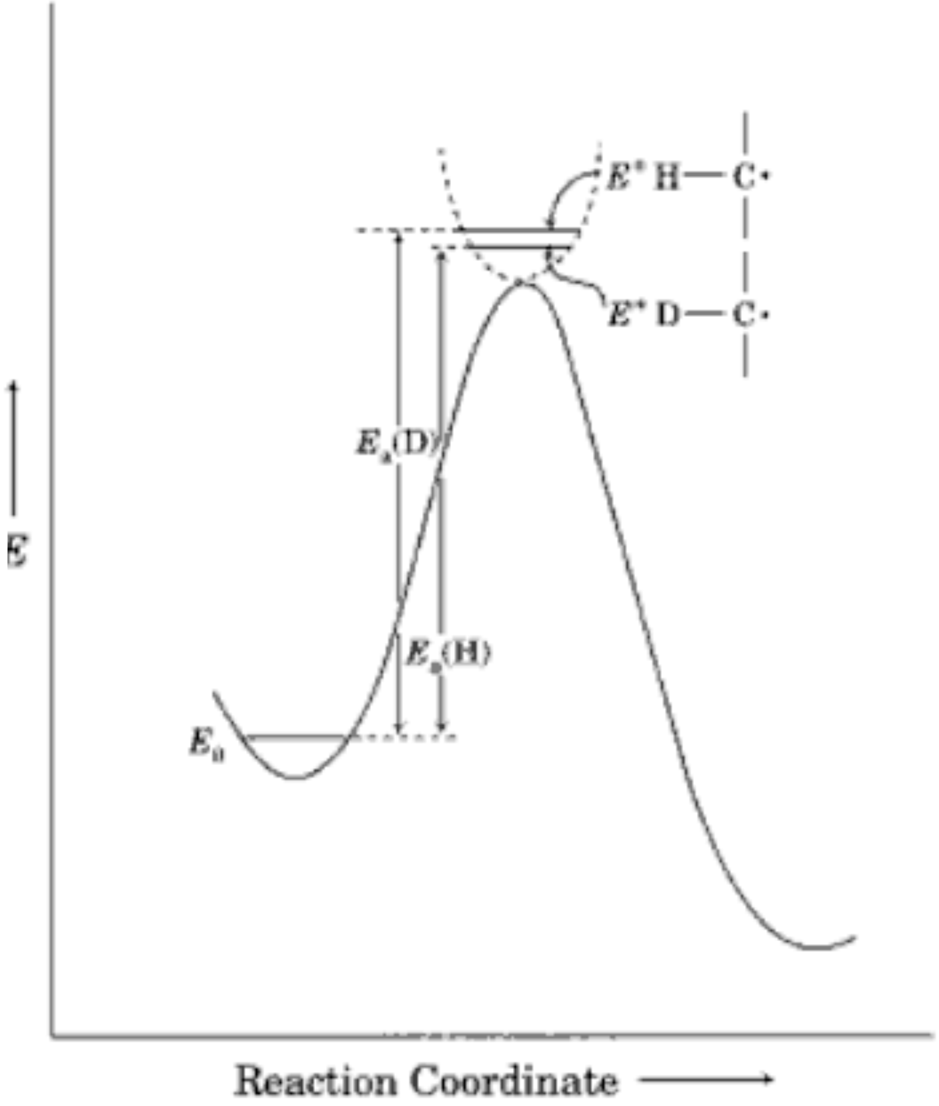


TABLE 6.4 Values of k_H/k_D for Gas Phase Bromination of α-Deuteriotoluene

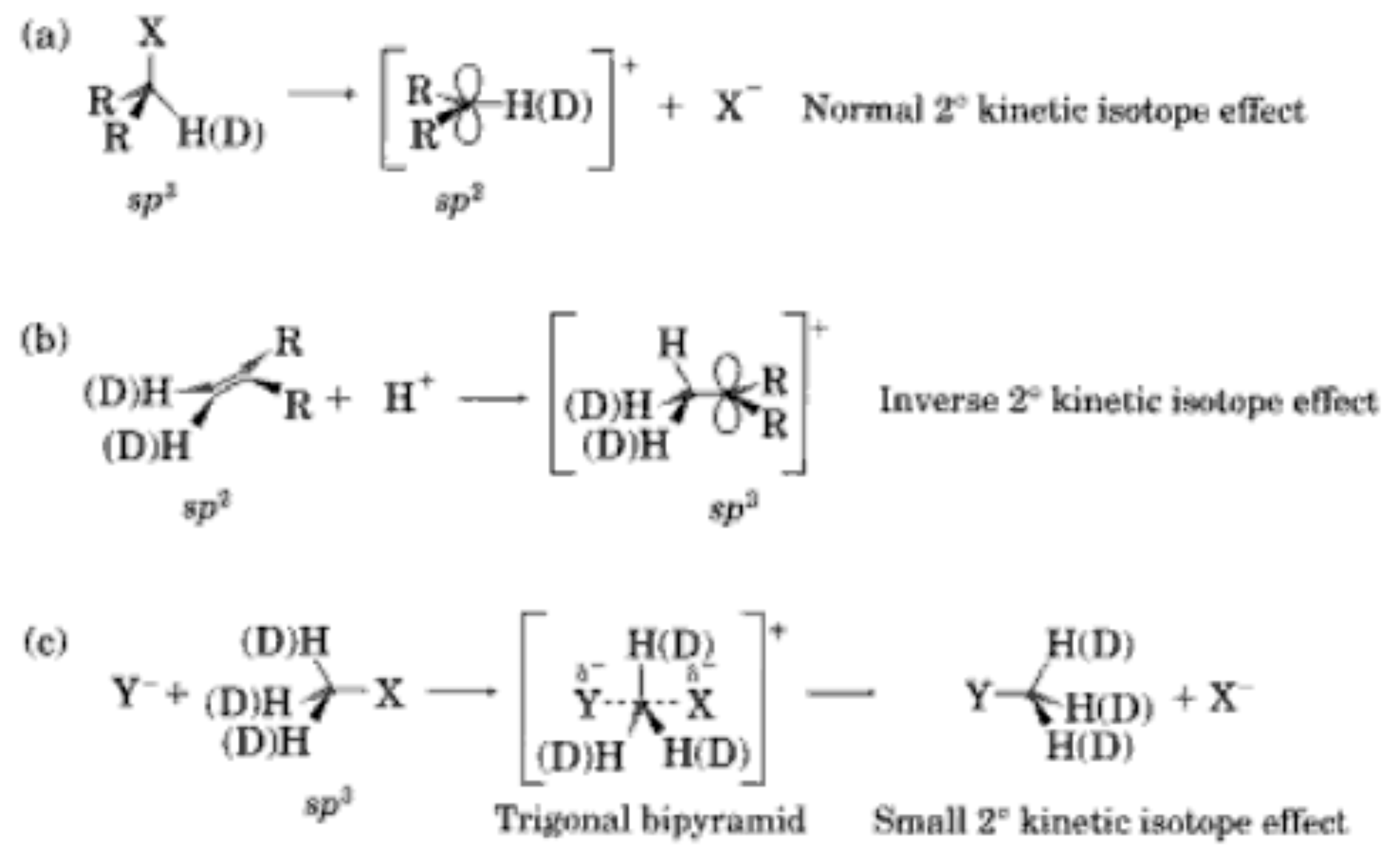
T (°C)	k_H/k_D
121	6.69
130	6.53
142	6.17
150	5.93
160	5.69

Source: Reference 144.

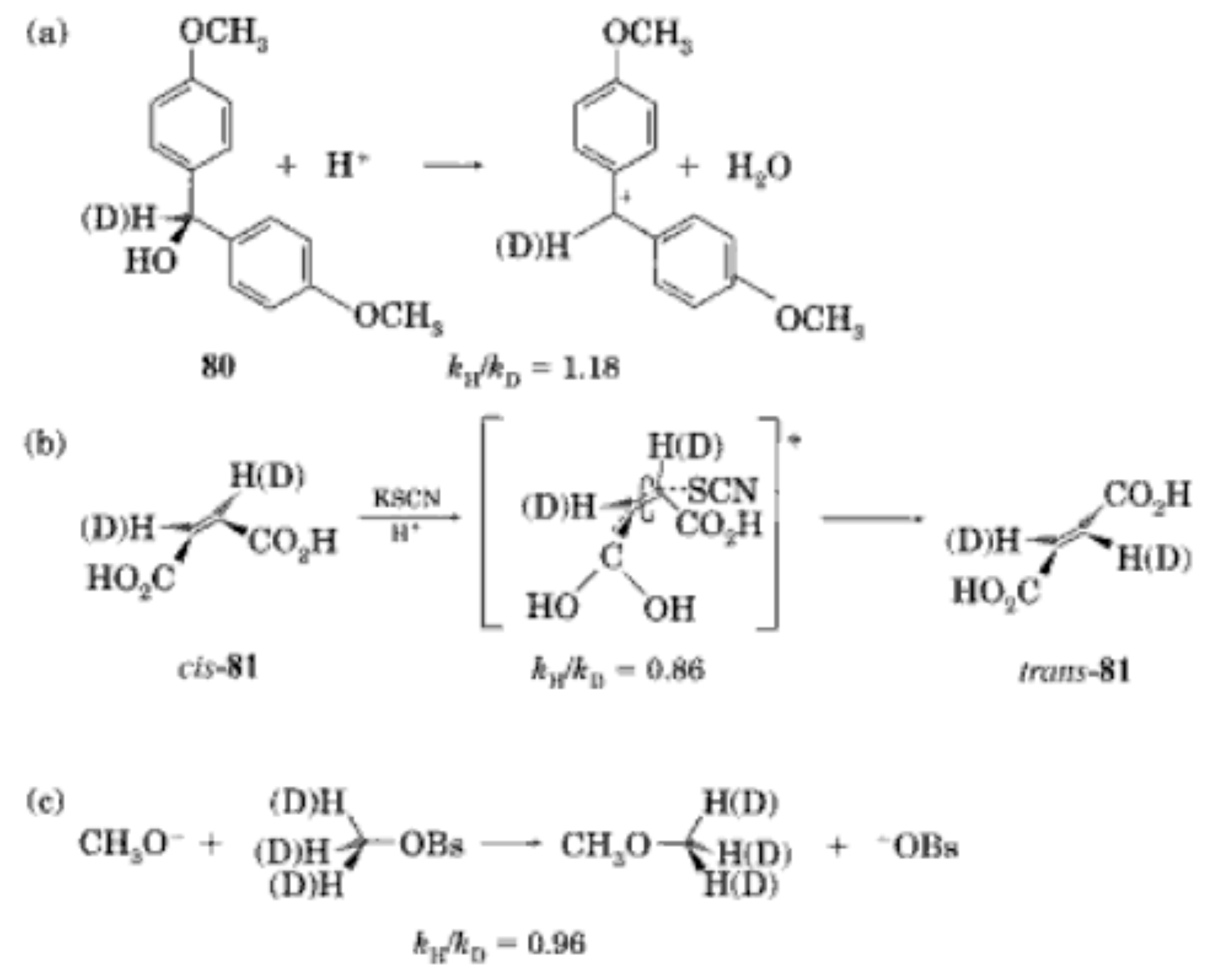


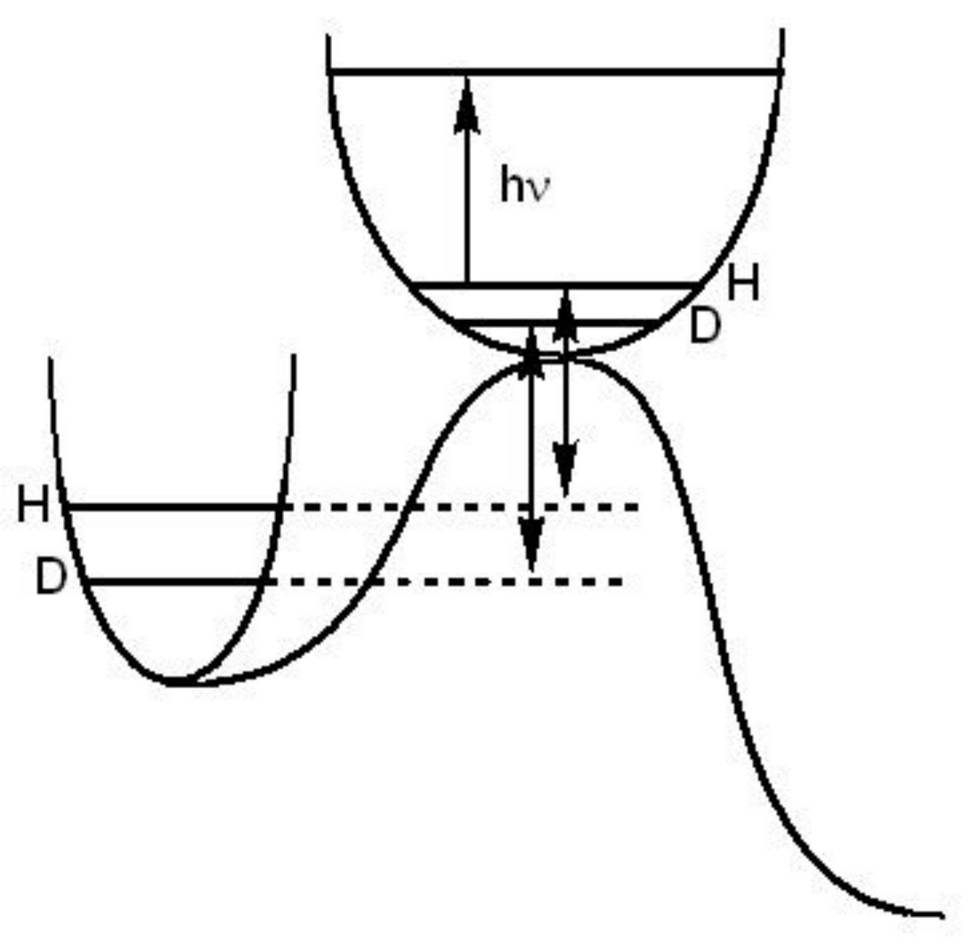


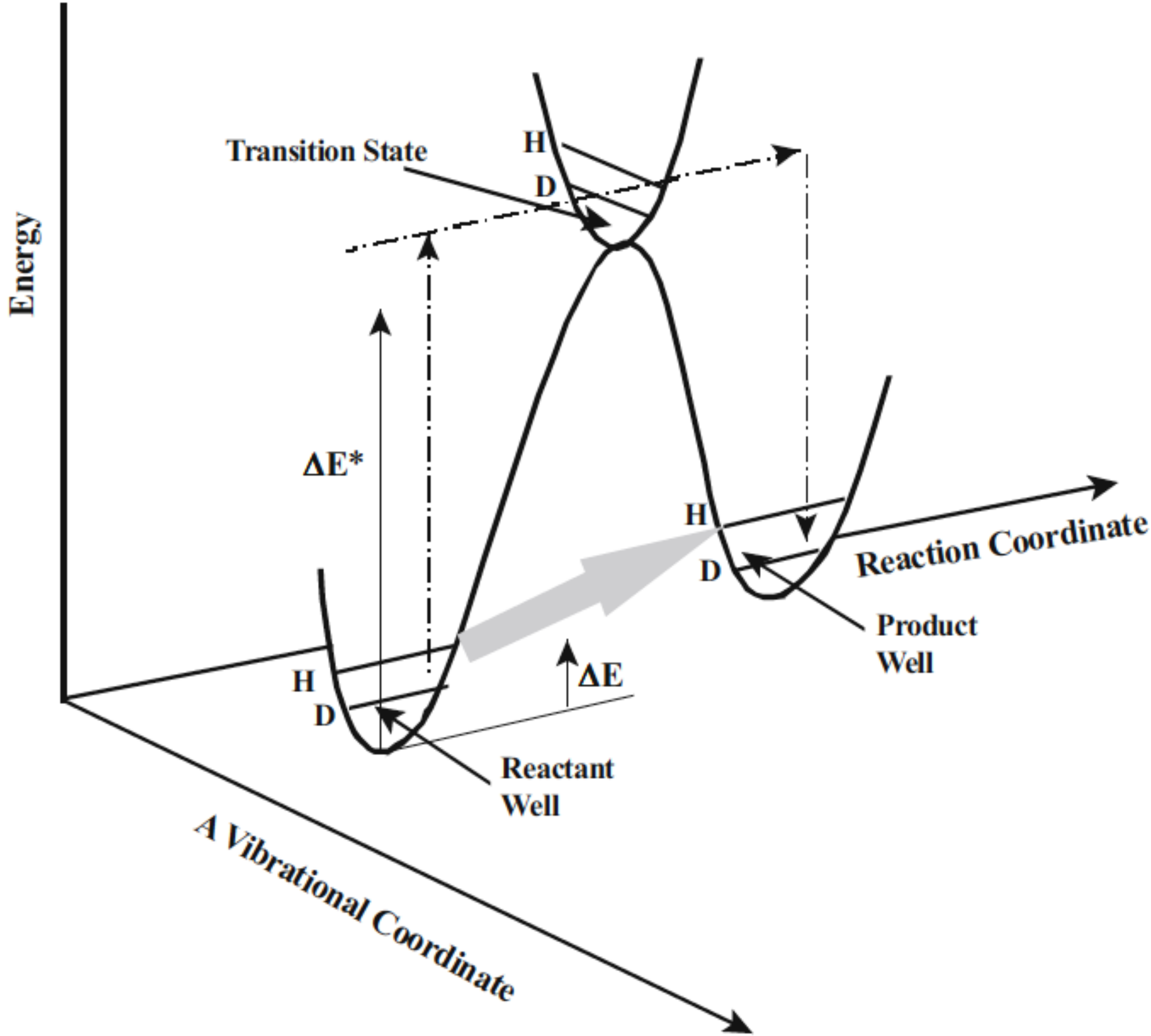
Tipos de Efeito secundário



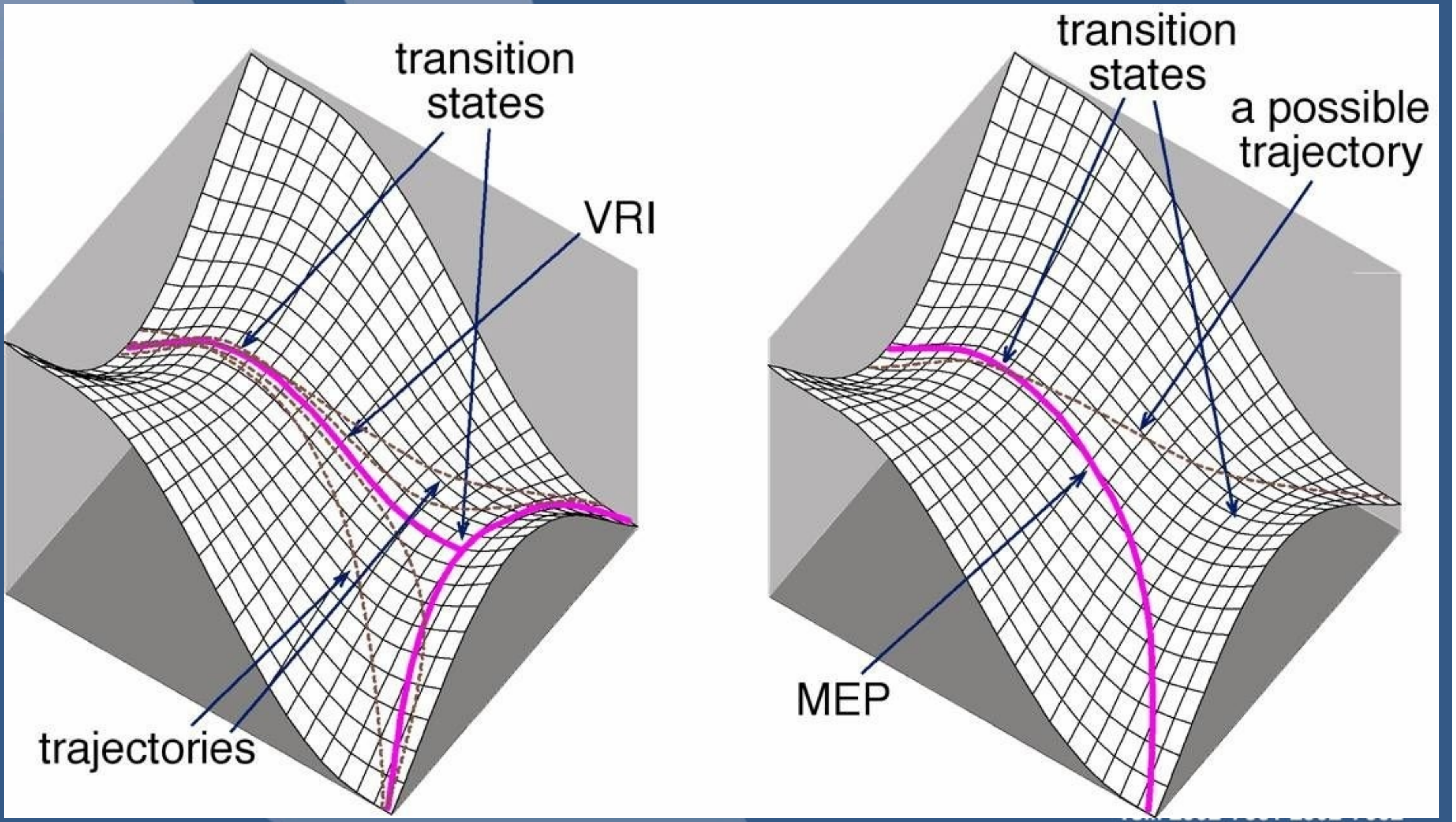
Efeito isotópico secundário



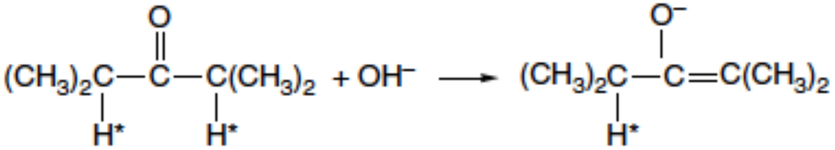
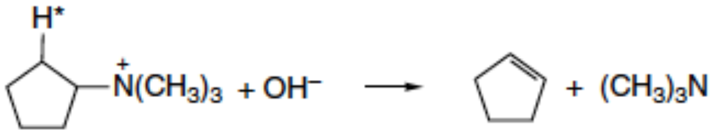
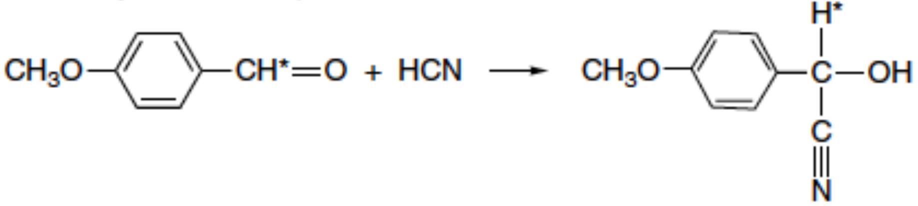
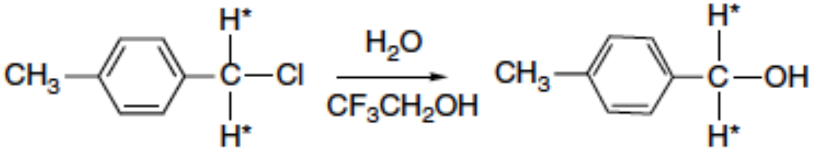
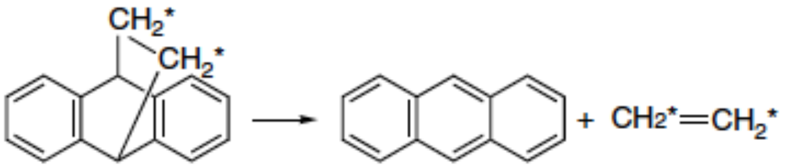

hν
H
D
H
D


Energy
Transition State
H
D
ΔE*
H
D
ΔE
Reactant
Well
H
D
Product
Well
Reaction Coordinate
A Vibrational Coordinate

Falhas na teoria do estado de transição



Scheme 3.4. Some Representative Kinetic Isotope Effects

Reaction	k_H/k_D (°C)
A. Primary kinetic isotope effects	
1[b] $PhCH_2-H^* + Br\cdot \longrightarrow Ph-CH_2\cdot + H^*-Br$	4.6 (77)
2[c]  $(CH_3)_2\underset{H^*}{C}-\overset{O}{\overset{\parallel}{C}}-\underset{H^*}{C}(CH_3)_2 + OH^- \longrightarrow (CH_3)_2\underset{H^*}{C}-\overset{O^-}{\overset{\vert}{C}}=C(CH_3)_2$	6.1 (25)
3[d] 	4.0 (191)
B. Secondary kinetic isotope effects	
4[e] 	0.73 (25)
5[f] 	1.30 (25)
6[g] 	1.37 (50)

a. Temperature of measurement is indicated in parentheses.

b. K. B. Wiberg and L. H. Slaugh, *J. Am. Chem. Soc.*, **80**, 3033 (1958).

c. R. A. Lynch, S. P. Vincenti, Y. T. Lin, L. D. Smucker, and S. C. Subba Rao, *J. Am. Chem. Soc.*, **94**, 8351 (1972).

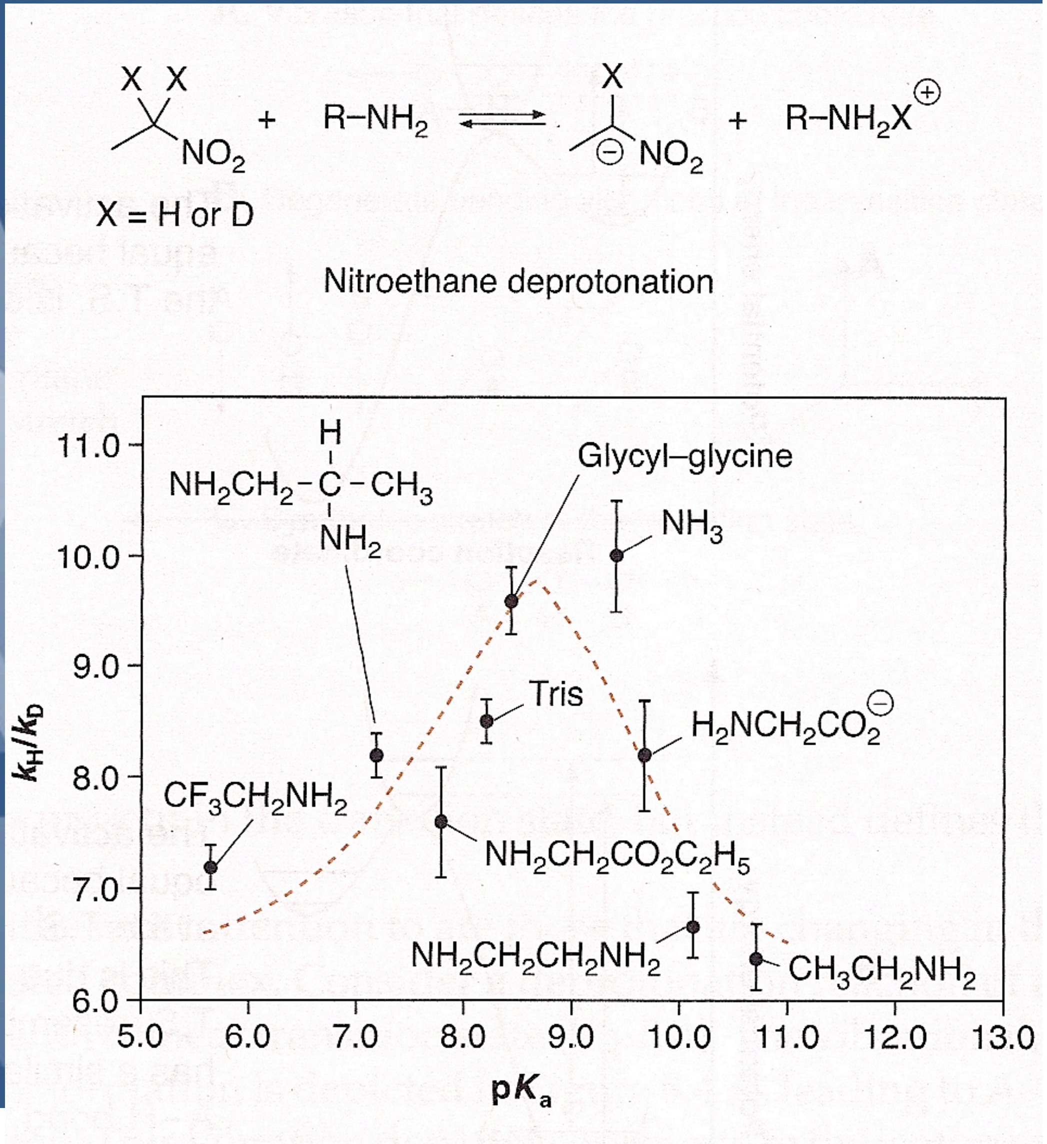
d. W. H. Saunders, Jr., and T. A. Ashe, *J. Am. Chem. Soc.*, **91**, 473 (1969).

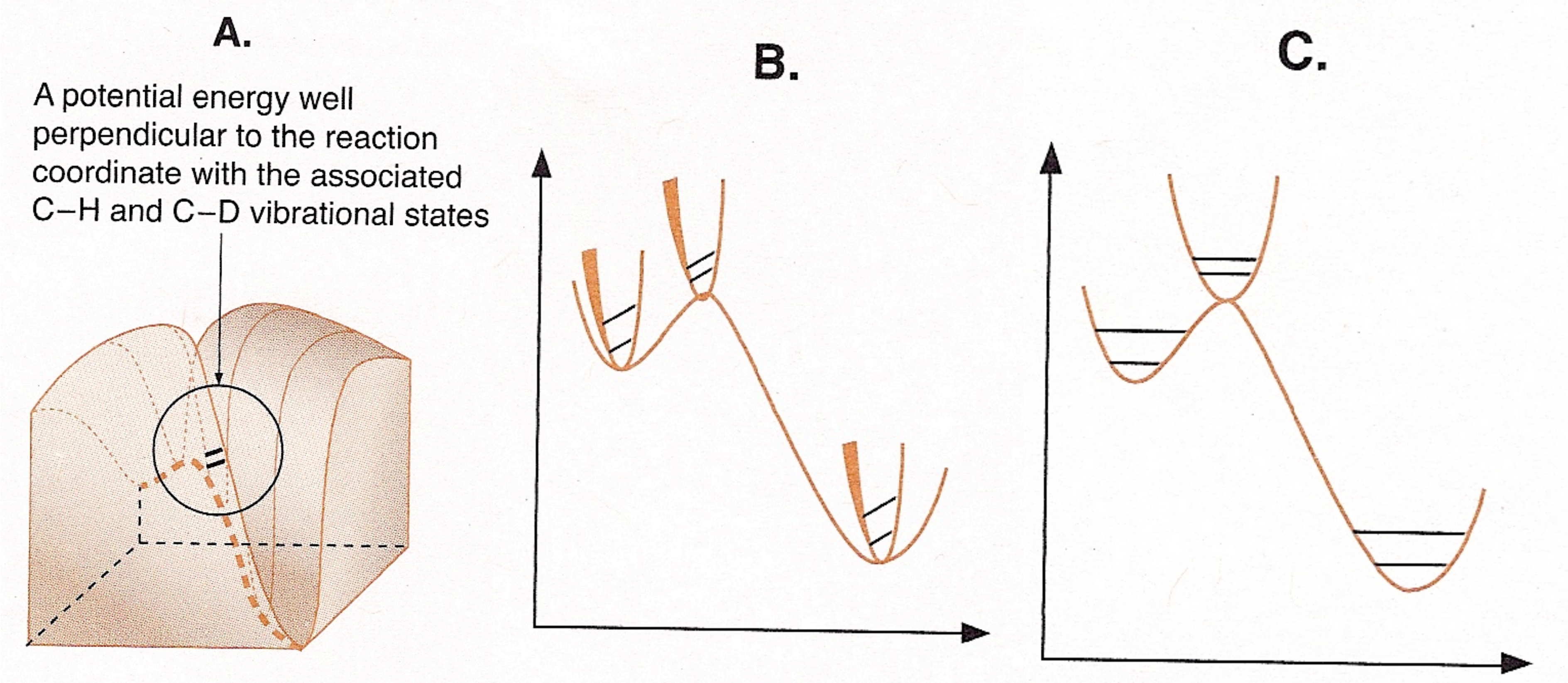
e. L. do Amaral, H. G. Bull, and E. H. Cordes, *J. Am. Chem. Soc.*, **94**, 7579 (1972).

f. V. J. Shiner, Jr., M. W. Rapp, and H. R. Pinnick, Jr., *J. Am. Chem. Soc.*, **92**, 232 (1970).

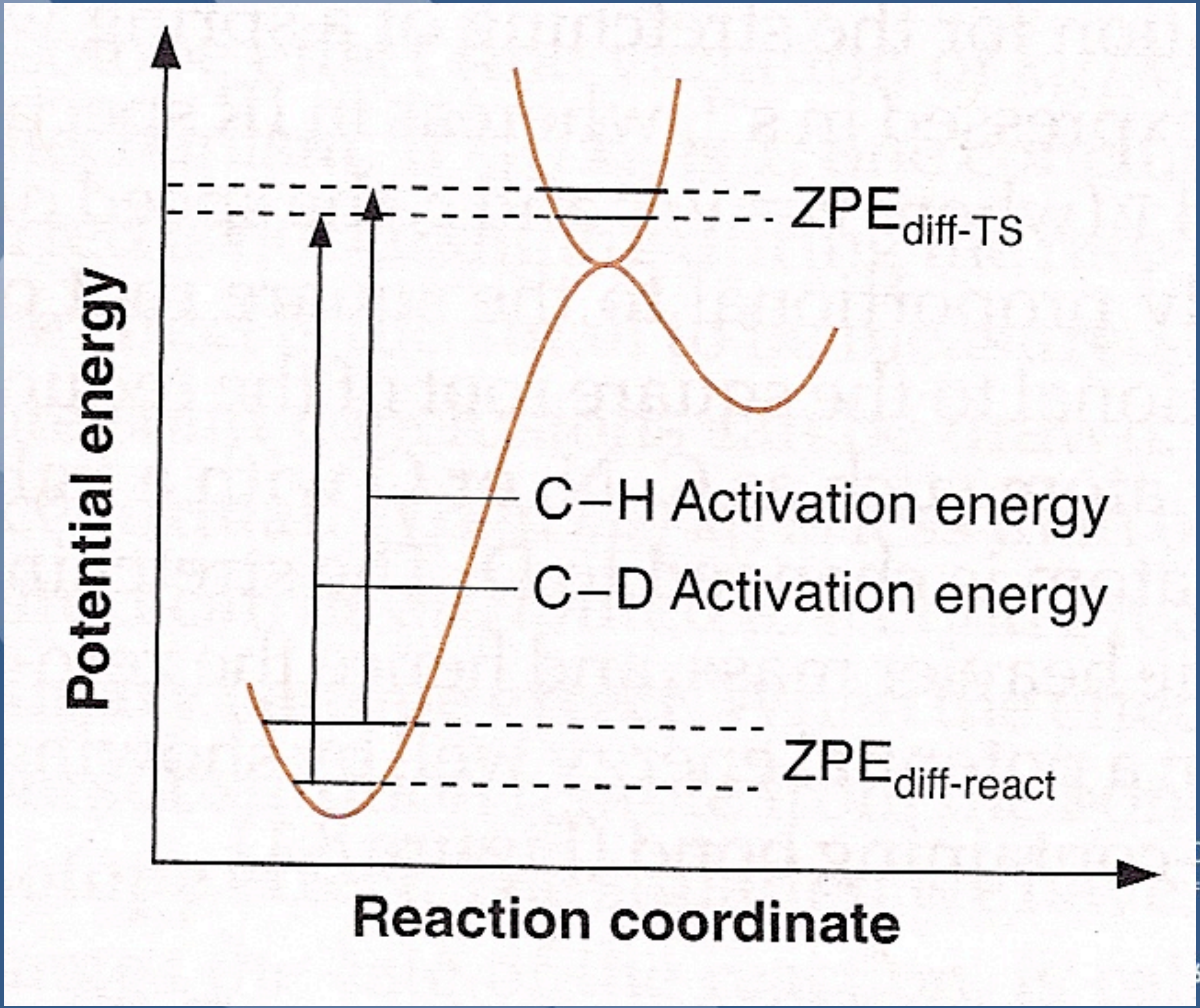
g. M. Taagepera and E. R. Thornton, *J. Am. Chem. Soc.*, **94**, 1168 (1972).

Efeito isotópico como indicação da geometria do ET_{cvr}



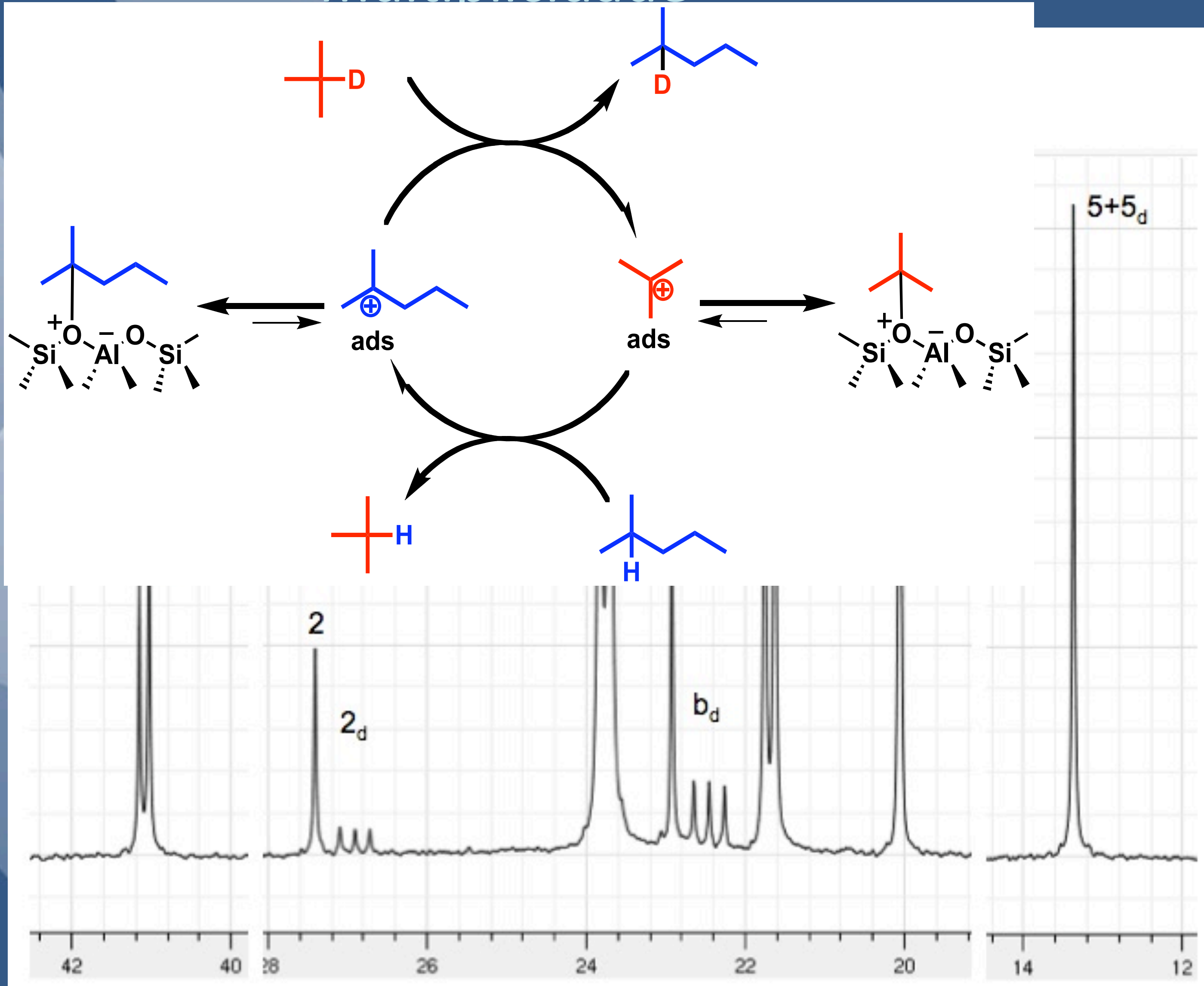


A potential energy well perpendicular to the reaction coordinate with the associated C–H and C–D vibrational states


Potential energy
ZPE$_{diff-TS}$
C–H Activation energy
C–D Activation energy
ZPE$_{diff-react}$
Reaction coordinate

Uso de isótopos: RMN ^{13}C permite determinar equilíbrio químico pela variação do δ devido à anarmonicidade e multiplicidade

Sido, Barbiche e Sommer Chem. Comm. 2010



Medindo efeitos de isótopos pesados na cinética com RMN em abundância natural

- Daniel A. Singleton (Texas A&M

Singleton& Thomas *JACS*, 1995, 117, 9357-8

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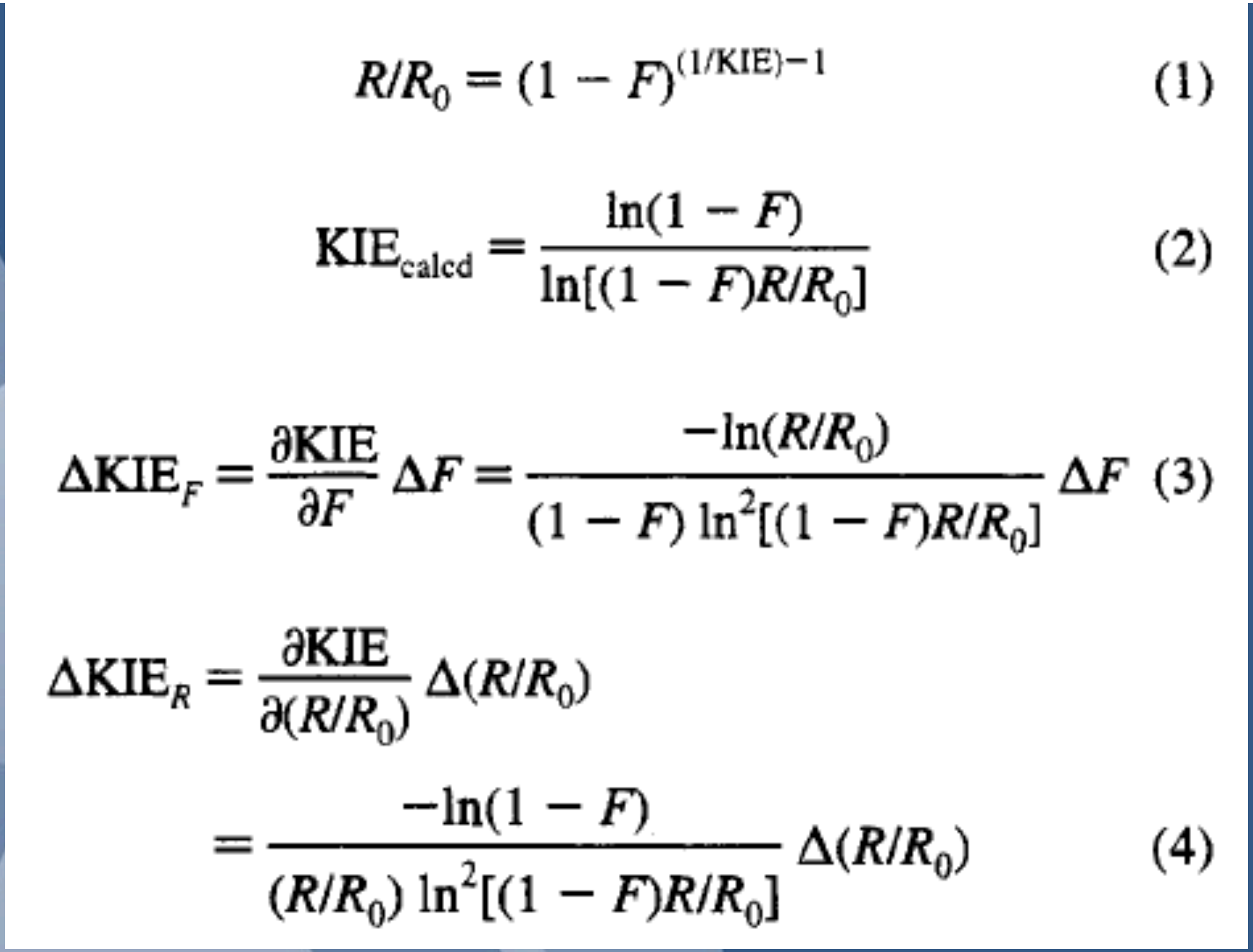

$$R/R_0 = (1 - F)^{(1/\mathrm{KIE})-1} \qquad (1)$$

$$\mathrm{KIE}_{\mathrm{calcd}} = \frac{\ln(1 - F)}{\ln[(1 - F)R/R_0]} \qquad (2)$$

$$\Delta\mathrm{KIE}_F = \frac{\partial\mathrm{KIE}}{\partial F}\Delta F = \frac{-\ln(R/R_0)}{(1 - F)\ln^2[(1 - F)R/R_0]}\Delta F \quad (3)$$

$$\Delta\mathrm{KIE}_R = \frac{\partial\mathrm{KIE}}{\partial(R/R_0)}\Delta(R/R_0)$$

$$= \frac{-\ln(1 - F)}{(R/R_0)\ln^2[(1 - F)R/R_0]}\Delta(R/R_0) \qquad (4)$$

- R/R_o = proporção do componente isotópico minoritário no material recuperado comparado ao material de partida
- F = conversão fracional
- KIE = efeito isotópico
- KIE = 1.05 corresponde a um enriquecimento de 25%do componente que reage mais lentamente a 99% de conversão

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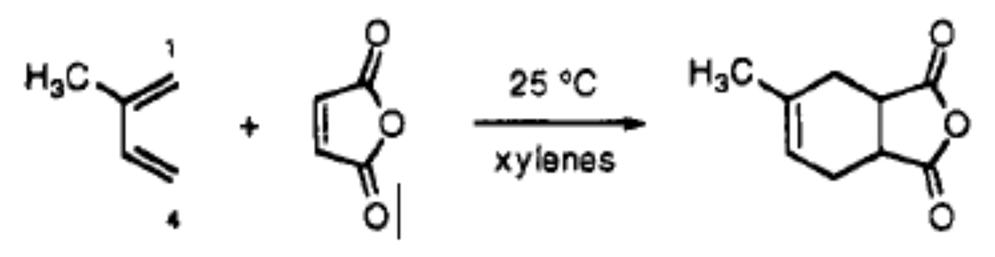
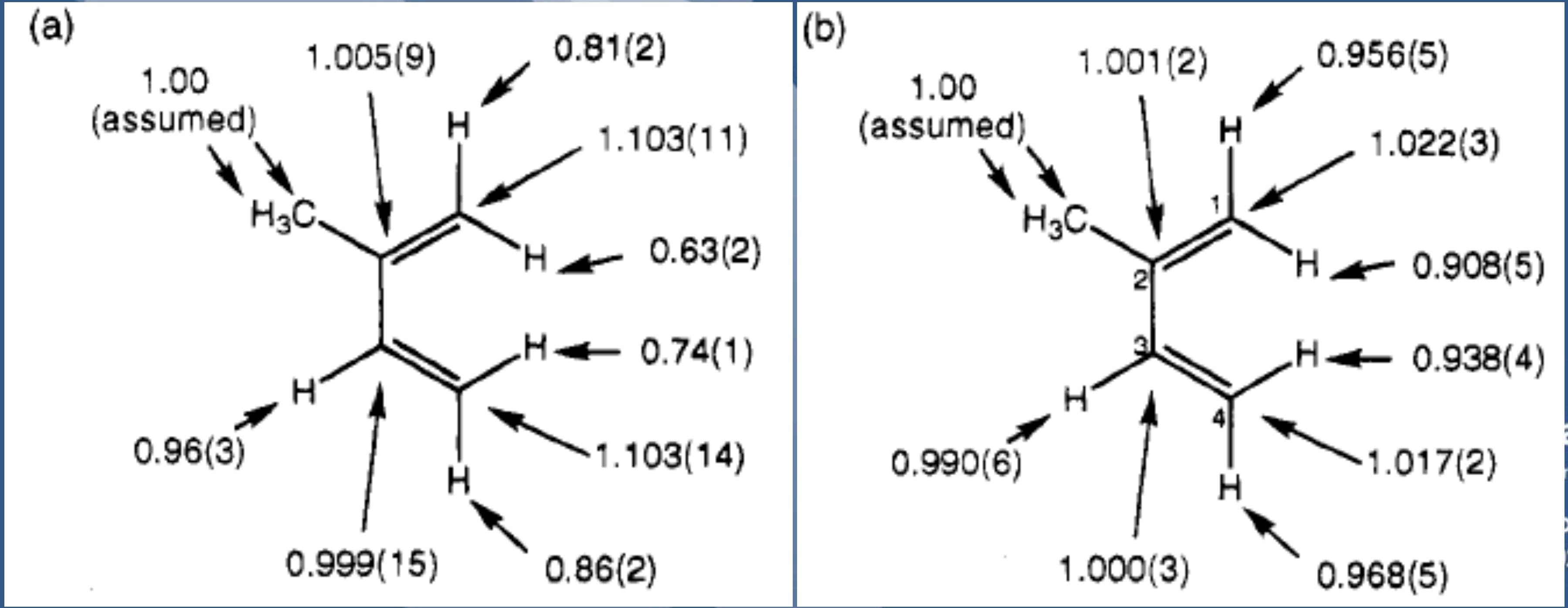
Resultados

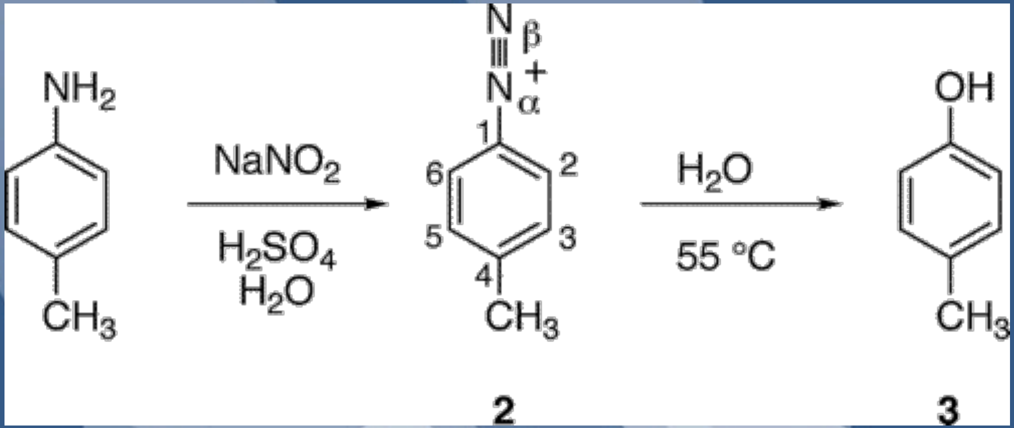


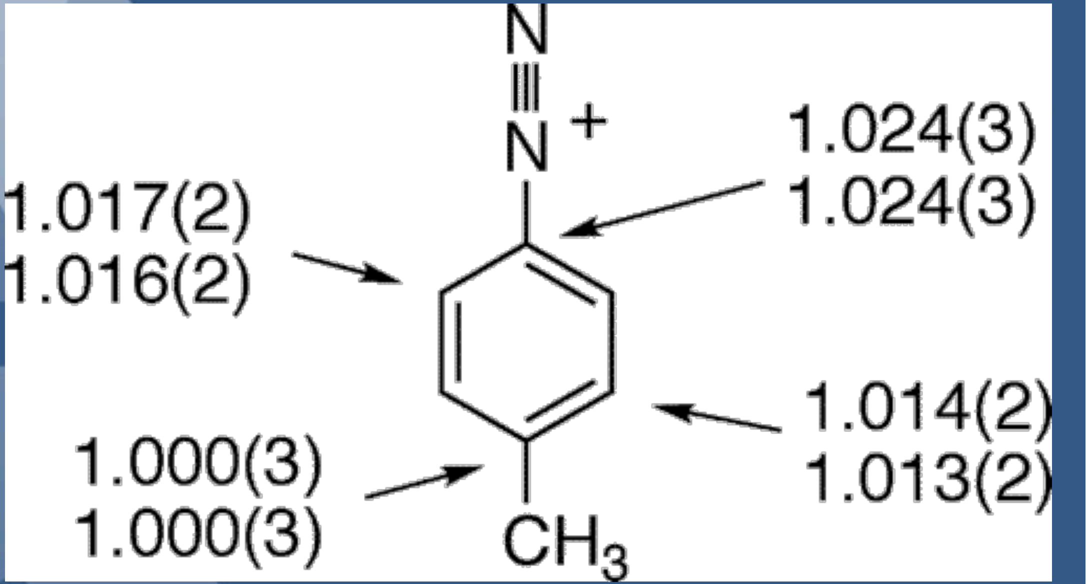
Composição isotópica de ^{2}H e ^{13}C no isopreno recuperado após 98.9 % de conversão

k_H/k_D k_{12C}/k_{13C}

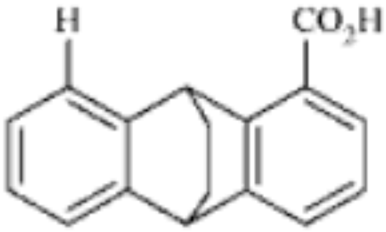


Decomposição de sais de diazônio



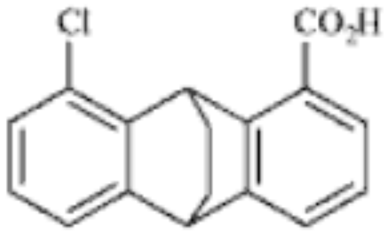


Efeito de Substituintes



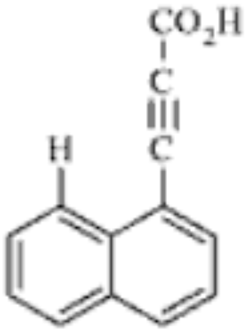
pK_a = 6.04 ± 0.03

85



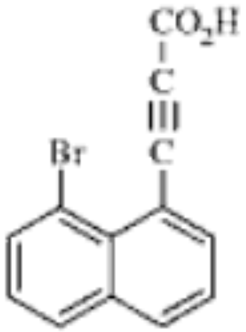
pK_a = 6.25 ± 0.02

86



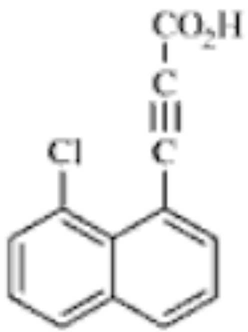
pK_a = 4.42

87



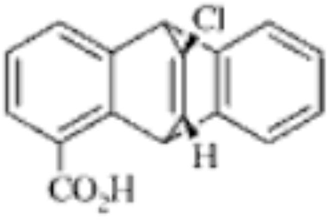
pK_a = 4.70

88

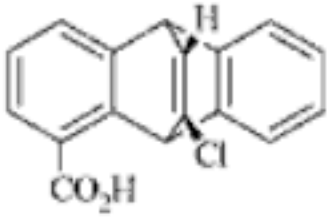


pK_a = 4.90

89



pK_a = 5.72 ± 0.01



pK_a = 5.90 ± 0.01

Valores de pKa e σ de ácidos, fenóis e anilinas

Grupo	*pKa Anilina*	*pKa Fenol*	*pKa Ácido*	σ	σ^+	σ^-
4-NH_2	6,16	10,3	4,92	- 0,66	-1,3	
3-NH_2	4,98	9,87	4,78	-0,16		
4-CH_3O	5,34	10,20	4,47	-0,27	-0,78	
3-CH_3O	4,24	9,65	4,09	+0,12		
4-CH_3	5,08	10,19	4,36	-0,14	-0,3	
3-CH_3	4,73	10,08	4,27			
H	4,63	9,95	4,19	0	0	0
4-Cl	4,15	9,38	3,98	+0,24	+0,11	
3-Cl	3,46	9,02	3,82	+0,37		
4-CN		7,95	3,55	+0,71		+0,99
3-CN	2,75	8,61	3,6	+0,62		
4-NO_2	1,0	7,14	3,41	+0,78		+1,23
3-NO_2	2,47	8,35	3,47	+0,71		

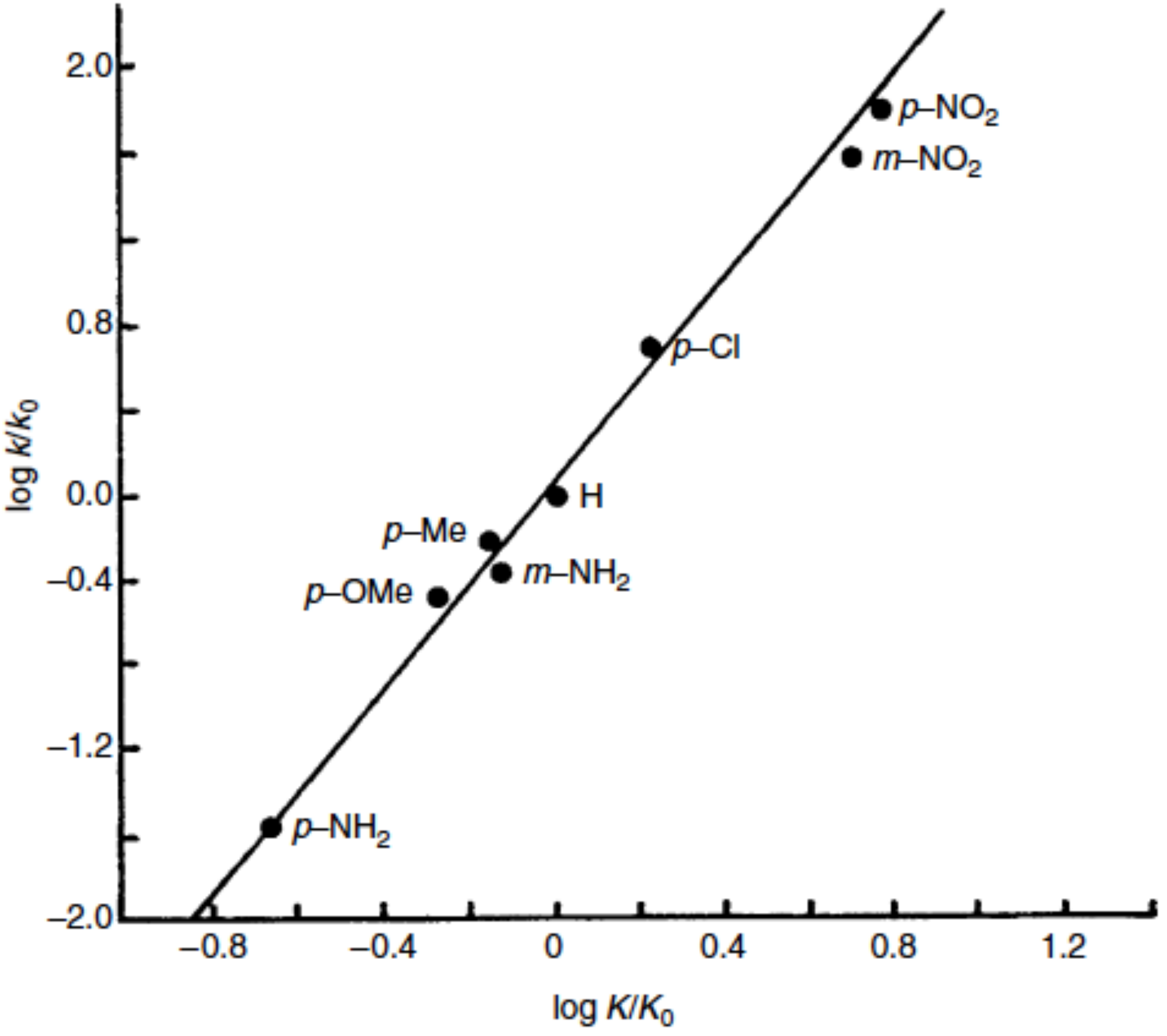


Fig. 3.25. Correlation of acid dissociation constants of benzoic acids with rates of basic hydrolysis of ethyl benzoates.

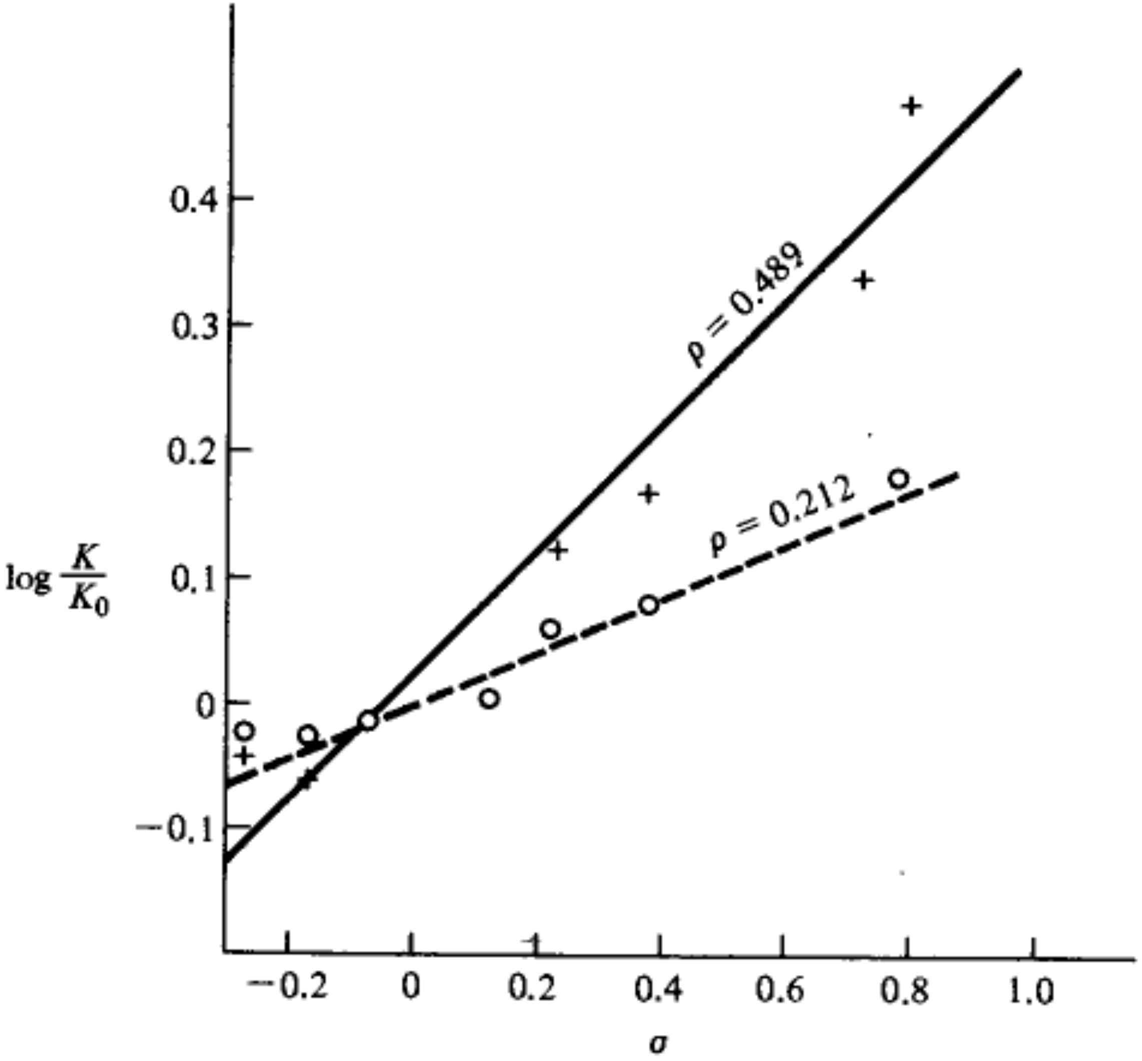


Figure 2.5 Plot of K/K_0 vs. σ constants for dissociation of X—$C_6H_4CH_2COOH$ (×) and of X—$C_6H_4CH_2CH_2COOH$ (○). The data are from Dippy, J. F. J.; Page, J. E. *J. Chem. Soc.* **1938,** 357, and the ρ values from a least-squares analysis of the data by Jaffe, H. H. *J. Chem. Phys.* **1953,** *21*, 415.

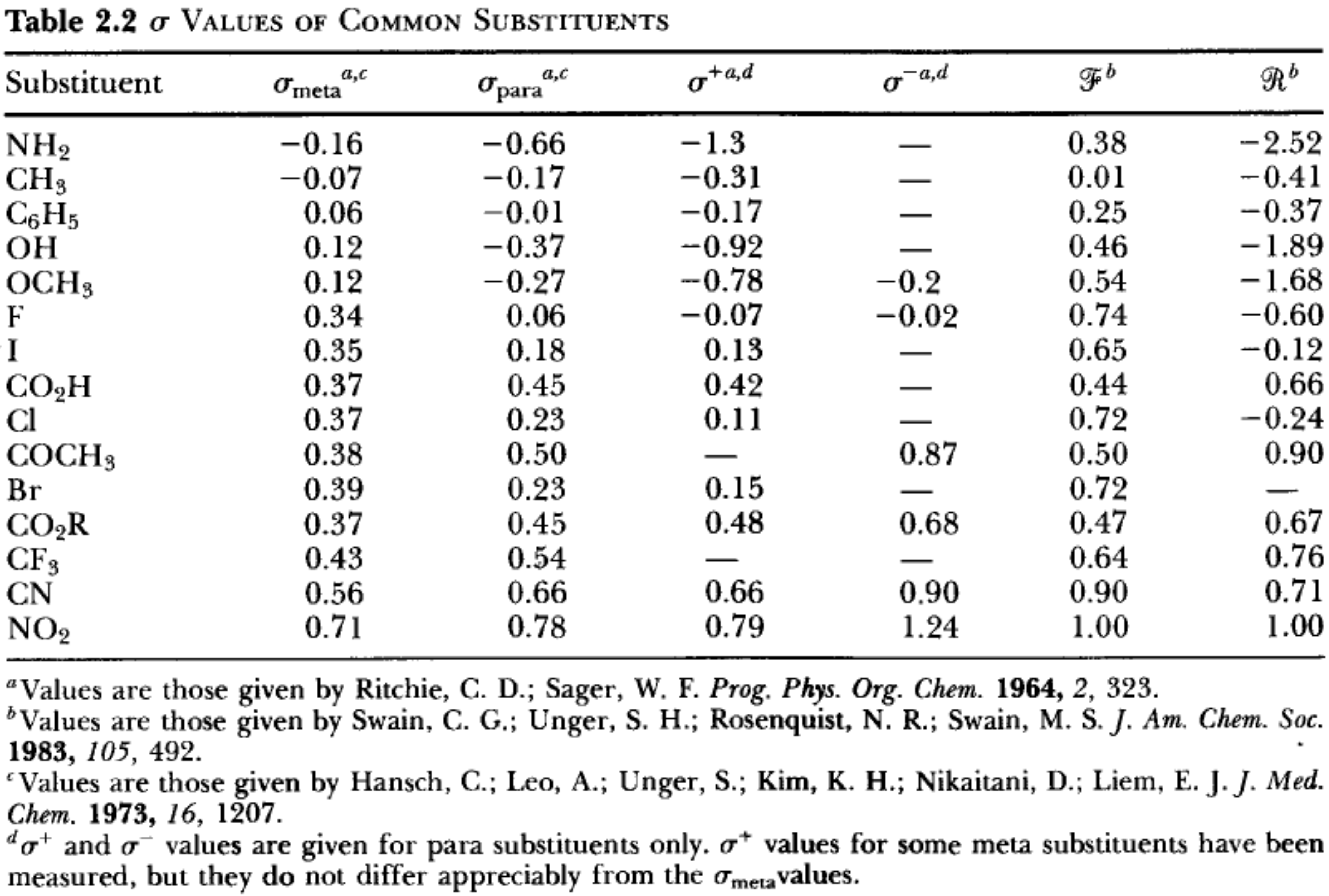


Table 2.2 σ VALUES OF COMMON SUBSTITUENTS

Substituent	$\sigma_{\text{meta}}{}^{a,c}$	$\sigma_{\text{para}}{}^{a,c}$	$\sigma^{+a,d}$	$\sigma^{-a,d}$	$\mathcal{F}^{b}$	$\mathcal{R}^{b}$
NH_2	−0.16	−0.66	−1.3	—	0.38	−2.52
CH_3	−0.07	−0.17	−0.31	—	0.01	−0.41
C_6H_5	0.06	−0.01	−0.17	—	0.25	−0.37
OH	0.12	−0.37	−0.92	—	0.46	−1.89
OCH_3	0.12	−0.27	−0.78	−0.2	0.54	−1.68
F	0.34	0.06	−0.07	−0.02	0.74	−0.60
I	0.35	0.18	0.13	—	0.65	−0.12
CO_2H	0.37	0.45	0.42	—	0.44	0.66
Cl	0.37	0.23	0.11	—	0.72	−0.24
$COCH_3$	0.38	0.50	—	0.87	0.50	0.90
Br	0.39	0.23	0.15	—	0.72	—
CO_2R	0.37	0.45	0.48	0.68	0.47	0.67
CF_3	0.43	0.54	—	—	0.64	0.76
CN	0.56	0.66	0.66	0.90	0.90	0.71
NO_2	0.71	0.78	0.79	1.24	1.00	1.00

[a] Values are those given by Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964,** *2*, 323.

[b] Values are those given by Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983,** *105*, 492.

[c] Values are those given by Hansch, C.; Leo, A.; Unger, S.; Kim, K. H.; Nikaitani, D.; Liem, E. J. *J. Med. Chem.* **1973,** *16*, 1207.

[d] σ^+ and σ^- values are given for para substituents only. σ^+ values for some meta substituents have been measured, but they do not differ appreciably from the σ_{meta} values.

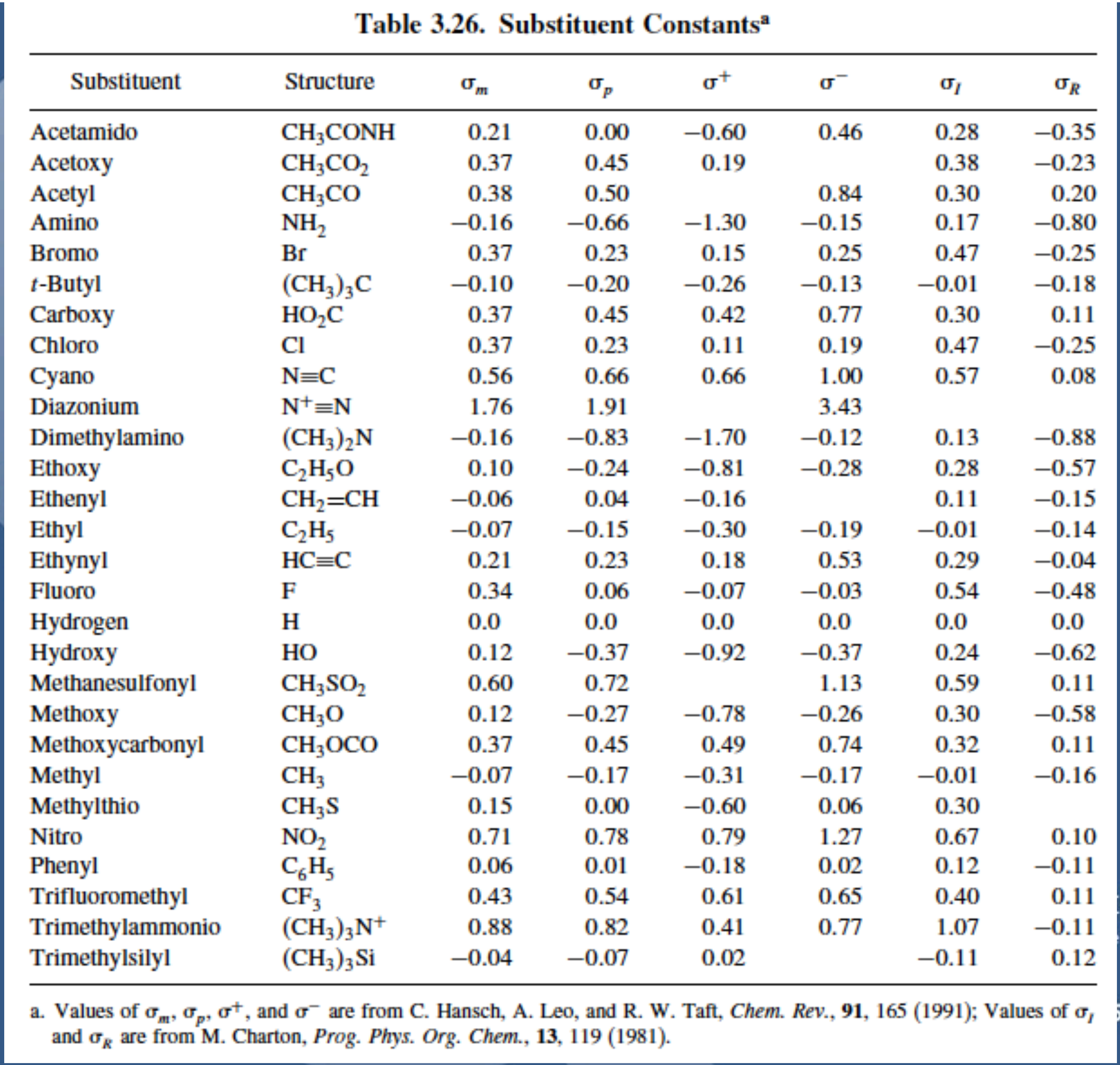
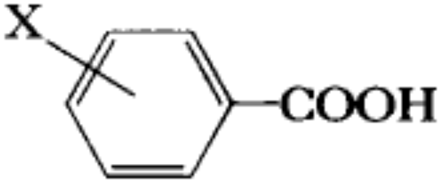
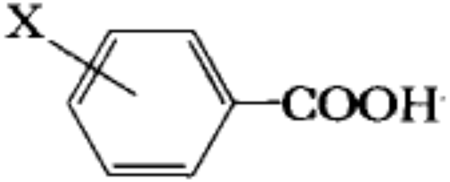
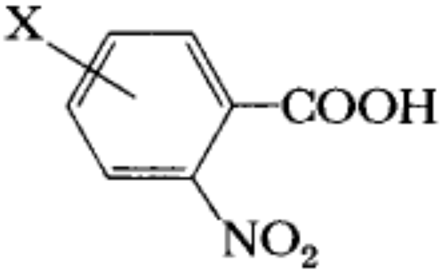
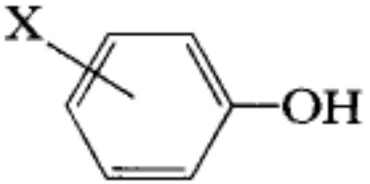


Table 3.26. Substituent Constants[a]

Substituent	Structure	σ_m	σ_p	σ^+	σ^-	σ_I	σ_R
Acetamido	CH_3CONH	0.21	0.00	−0.60	0.46	0.28	−0.35
Acetoxy	CH_3CO_2	0.37	0.45	0.19		0.38	−0.23
Acetyl	CH_3CO	0.38	0.50		0.84	0.30	0.20
Amino	NH_2	−0.16	−0.66	−1.30	−0.15	0.17	−0.80
Bromo	Br	0.37	0.23	0.15	0.25	0.47	−0.25
t-Butyl	$(CH_3)_3C$	−0.10	−0.20	−0.26	−0.13	−0.01	−0.18
Carboxy	HO_2C	0.37	0.45	0.42	0.77	0.30	0.11
Chloro	Cl	0.37	0.23	0.11	0.19	0.47	−0.25
Cyano	$N{\equiv}C$	0.56	0.66	0.66	1.00	0.57	0.08
Diazonium	$N^+{\equiv}N$	1.76	1.91		3.43		
Dimethylamino	$(CH_3)_2N$	−0.16	−0.83	−1.70	−0.12	0.13	−0.88
Ethoxy	C_2H_5O	0.10	−0.24	−0.81	−0.28	0.28	−0.57
Ethenyl	$CH_2{=}CH$	−0.06	0.04	−0.16		0.11	−0.15
Ethyl	C_2H_5	−0.07	−0.15	−0.30	−0.19	−0.01	−0.14
Ethynyl	$HC{\equiv}C$	0.21	0.23	0.18	0.53	0.29	−0.04
Fluoro	F	0.34	0.06	−0.07	−0.03	0.54	−0.48
Hydrogen	H	0.0	0.0	0.0	0.0	0.0	0.0
Hydroxy	HO	0.12	−0.37	−0.92	−0.37	0.24	−0.62
Methanesulfonyl	CH_3SO_2	0.60	0.72		1.13	0.59	0.11
Methoxy	CH_3O	0.12	−0.27	−0.78	−0.26	0.30	−0.58
Methoxycarbonyl	CH_3OCO	0.37	0.45	0.49	0.74	0.32	0.11
Methyl	CH_3	−0.07	−0.17	−0.31	−0.17	−0.01	−0.16
Methylthio	CH_3S	0.15	0.00	−0.60	0.06	0.30	
Nitro	NO_2	0.71	0.78	0.79	1.27	0.67	0.10
Phenyl	C_6H_5	0.06	0.01	−0.18	0.02	0.12	−0.11
Trifluoromethyl	CF_3	0.43	0.54	0.61	0.65	0.40	0.11
Trimethylammonio	$(CH_3)_3N^+$	0.88	0.82	0.41	0.77	1.07	−0.11
Trimethylsilyl	$(CH_3)_3Si$	−0.04	−0.07	0.02		−0.11	0.12

a. Values of σ_m, σ_p, σ^+, and σ^- are from C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, **91**, 165 (1991); Values of σ_I and σ_R are from M. Charton, *Prog. Phys. Org. Chem.*, **13**, 119 (1981).

Table 2.3 ρ VALUES FOR ACID DISSOCIATIONS[a]

Acid	Solvent	Temperature (°C)	ρ
	H_2O	25	1.00
	C_2H_5OH	25	1.957
	H_2O	25	0.905
	H_2O	25	2.113

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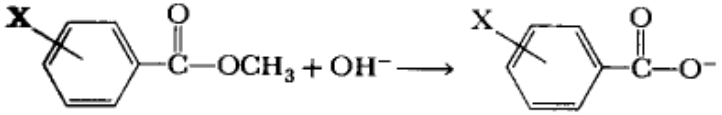
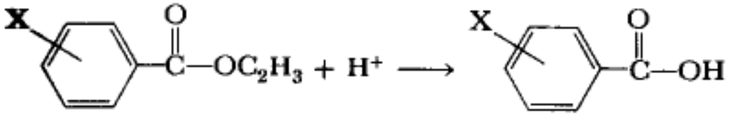
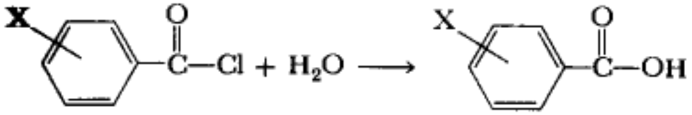
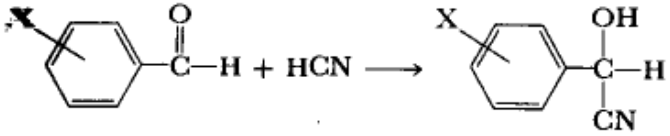
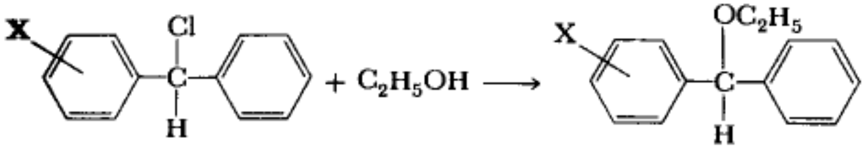
[a] Reprinted with permission from Jaffe, H. H. *Chem. Rev.* **1953,** *53,* 191. Copyright 1953 American Chemical Society. Refer to this source for more complete data.

Table 2.4 ρ Values Derived from Rates of Heterolytic Reactions[a]

Reaction	Solvent	Temperature (°C)	ρ
	60% acetone	25	2.229
	60% acetone	100	0.106
	50% acetone	0	0.797
	95% ethanol	20	2.329
	ethanol	25	−5.090

[a] Reprinted with permission from Jaffe, H. H. *Chem. Rev.* **1953,** *53,* 191. Copyright 1953 American Chemical Society. Refer to this source for more complete data.

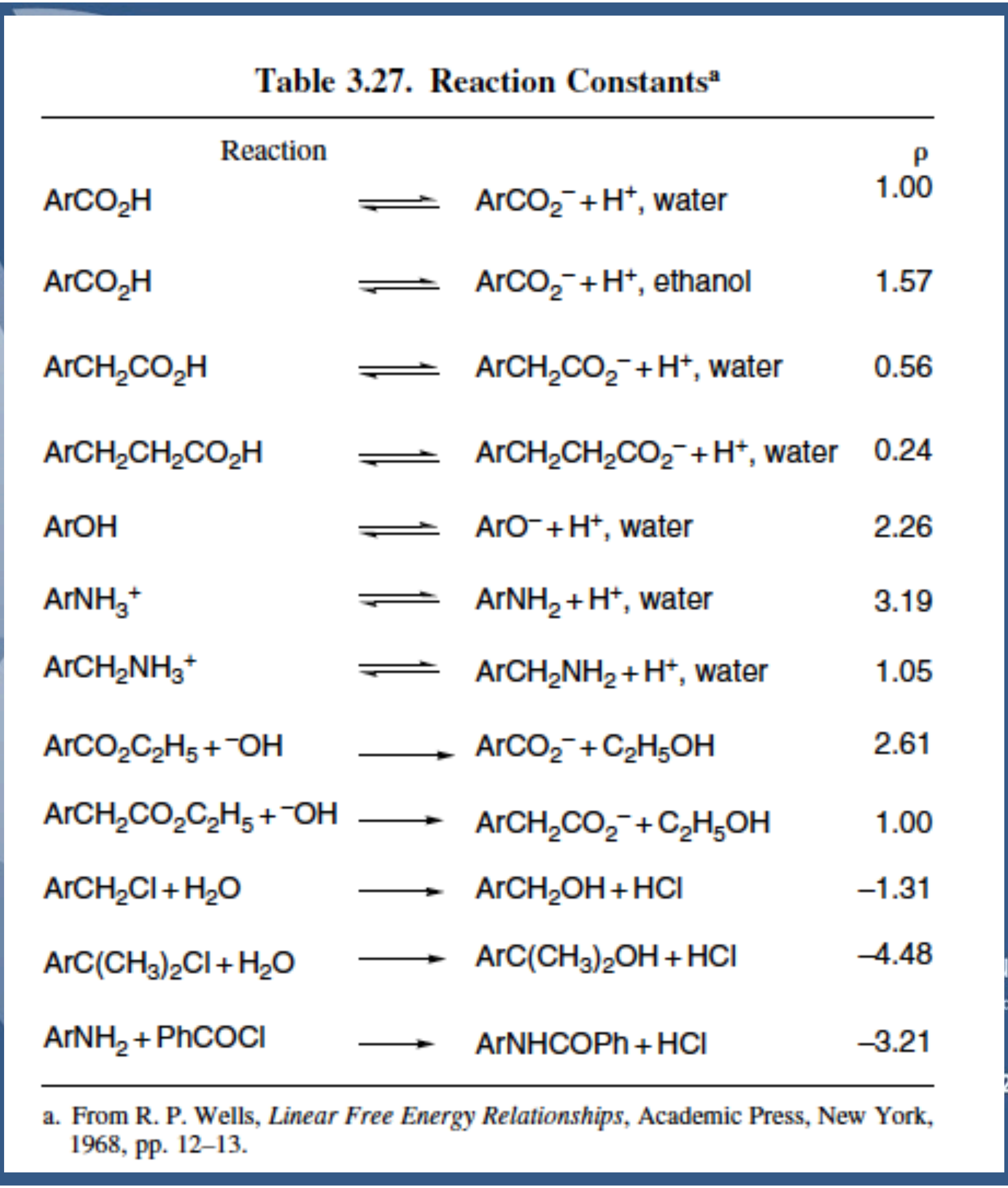
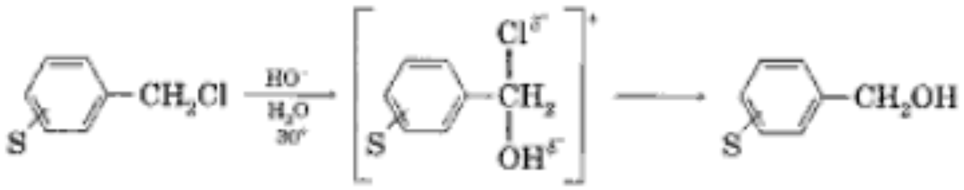


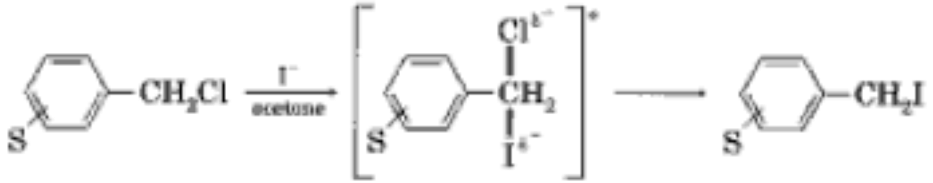
Table 3.27. Reaction Constants[a]

Reaction			ρ
$ArCO_2H$	$\rightleftharpoons$	$ArCO_2^- + H^+$, water	1.00
$ArCO_2H$	$\rightleftharpoons$	$ArCO_2^- + H^+$, ethanol	1.57
$ArCH_2CO_2H$	$\rightleftharpoons$	$ArCH_2CO_2^- + H^+$, water	0.56
$ArCH_2CH_2CO_2H$	$\rightleftharpoons$	$ArCH_2CH_2CO_2^- + H^+$, water	0.24
$ArOH$	$\rightleftharpoons$	$ArO^- + H^+$, water	2.26
$ArNH_3^+$	$\rightleftharpoons$	$ArNH_2 + H^+$, water	3.19
$ArCH_2NH_3^+$	$\rightleftharpoons$	$ArCH_2NH_2 + H^+$, water	1.05
$ArCO_2C_2H_5 + {}^-OH$	$\rightarrow$	$ArCO_2^- + C_2H_5OH$	2.61
$ArCH_2CO_2C_2H_5 + {}^-OH$	$\rightarrow$	$ArCH_2CO_2^- + C_2H_5OH$	1.00
$ArCH_2Cl + H_2O$	$\rightarrow$	$ArCH_2OH + HCl$	–1.31
$ArC(CH_3)_2Cl + H_2O$	$\rightarrow$	$ArC(CH_3)_2OH + HCl$	–4.48
$ArNH_2 + PhCOCl$	$\rightarrow$	$ArNHCOPh + HCl$	–3.21

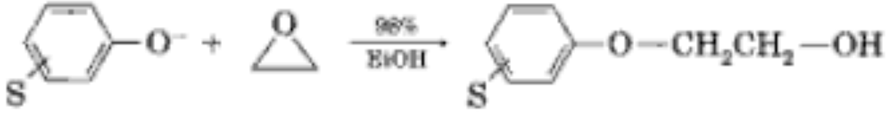
a. From R. P. Wells, *Linear Free Energy Relationships*, Academic Press, New York, 1968, pp. 12–13.



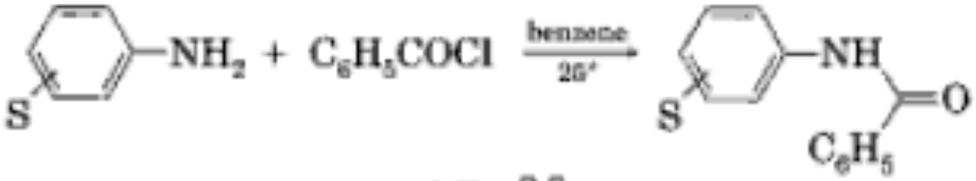
$\rho = -0.3$



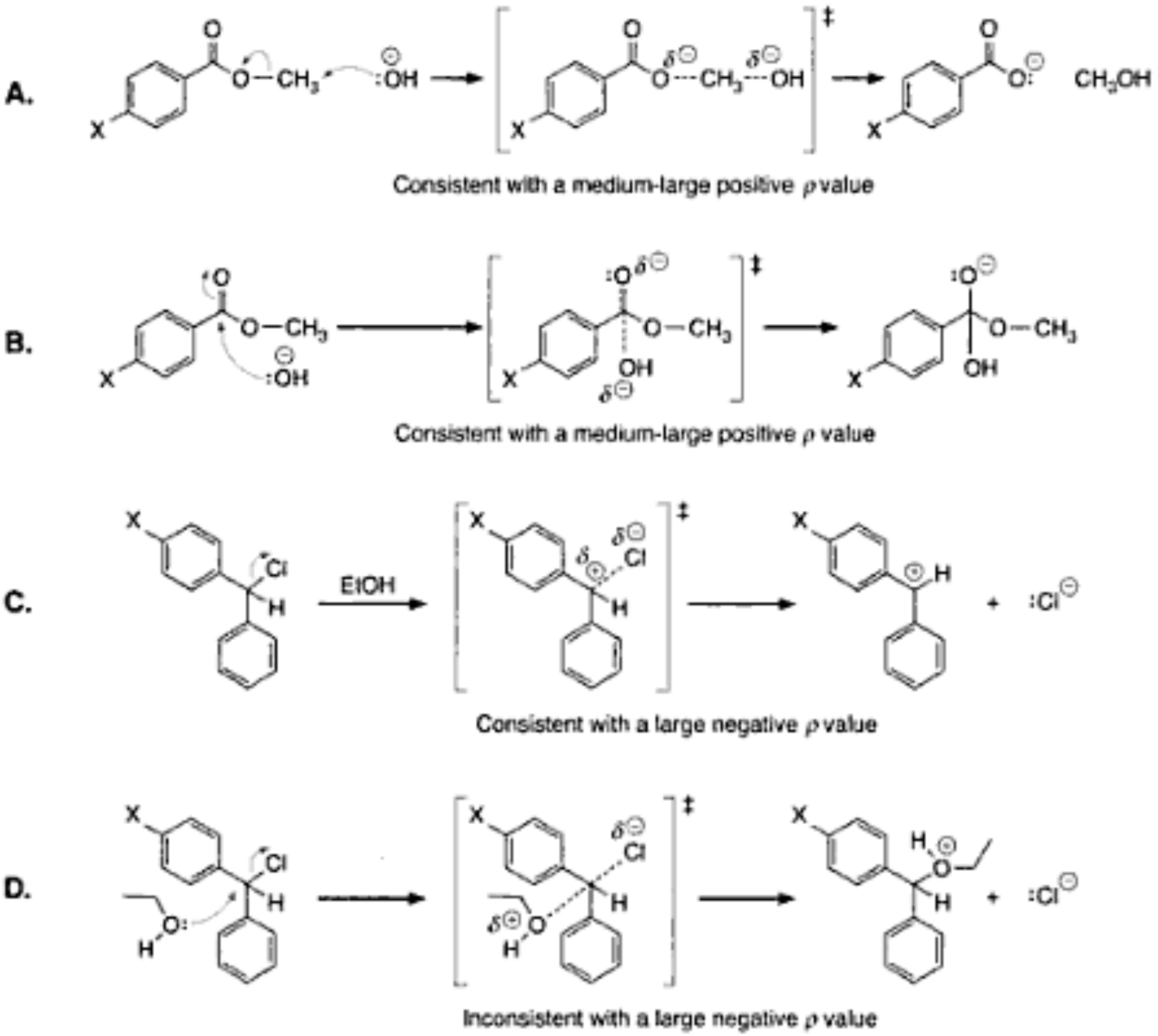
$\rho = +0.8$



$\rho = -0.95\ (70°)$



$\rho = -2.8$



Consistent with a medium-large positive ρ value

Consistent with a medium-large positive ρ value

Consistent with a large negative ρ value

Inconsistent with a large negative ρ value

Figure 8.12
Examples of reactions and expected ρ values. A ρ value of 2.33 for the reactions shown in A and B does not distinguish between these two mechanistic alternatives. A ρ value of –5.09 for the first step of the substitution reaction given in C and D supports alternative C.

Table 8.6
A Summary of the Most Common LFERs Used*

LFER	Substituent constant	Reference reaction	Used to study	Reaction constant and its meaning relative to the reference reaction
Hammett	σ	Ionization of benzoic acid	Inductive effects	$\rho > 1$, more sensitive $0 < \rho < 1$, less sensitive $\rho = 0$, not sensitive $\rho < 0$, positive charge created
Hammett	σ^-	Ionization of phenol	Resonance in addition to induction	Same as above
Hammett	σ^+	Ionization of phenyldimethyl chloromethane	Resonance in addition to induction	Same as above
Taft	E_s	Hydrolysis of methyl esters	Steric size	$\delta > 1$, more sensitive $\delta < 1$, less sensitive
Grunwald–Winstein	Y	Ionization of t-BuCl in 80:20 EtOH/H_2O	Ionizing power of solvent	$m > 1$, more sensitive $m < 1$, less sensitive
Swain–Scott	n	S_N2 reaction of methyl iodide in water	Nucleophilicity	$s > 1$, more sensitive $s < 1$, less sensitive
Brønsted	pK_a	Acidity in water	Nucleophilicity	$\beta_{Nuc} > 1$, more sensitive $\beta_{Nuc} < 1$, less sensitive
Brønsted	pK_a	Acidity in water	Leaving group departure	$\beta_{LG} > -1$, more sensitive $\beta_{LG} < -1$, less sensitive
Brønsted	pK_a	Acidity in water	Acid catalysis	$\alpha > 1$, more sensitive $\alpha < 1$, less sensitive
Brønsted	pK_a	Acidity in water	Basic catalysis	$\beta > 1$, more sensitive $\beta < 1$, less sensitive

*Not all of the LFERs discussed in the text are included in Table 8.6. Only those most likely to be encountered in modern research are included.

Swain-Lupton

- Relação com dois parâmetros
  - – Efeito de campo (F)
  - – Efeito de Ressonância (R)

$$\log\left(\frac{k}{k_0}\right) = fF + rR$$

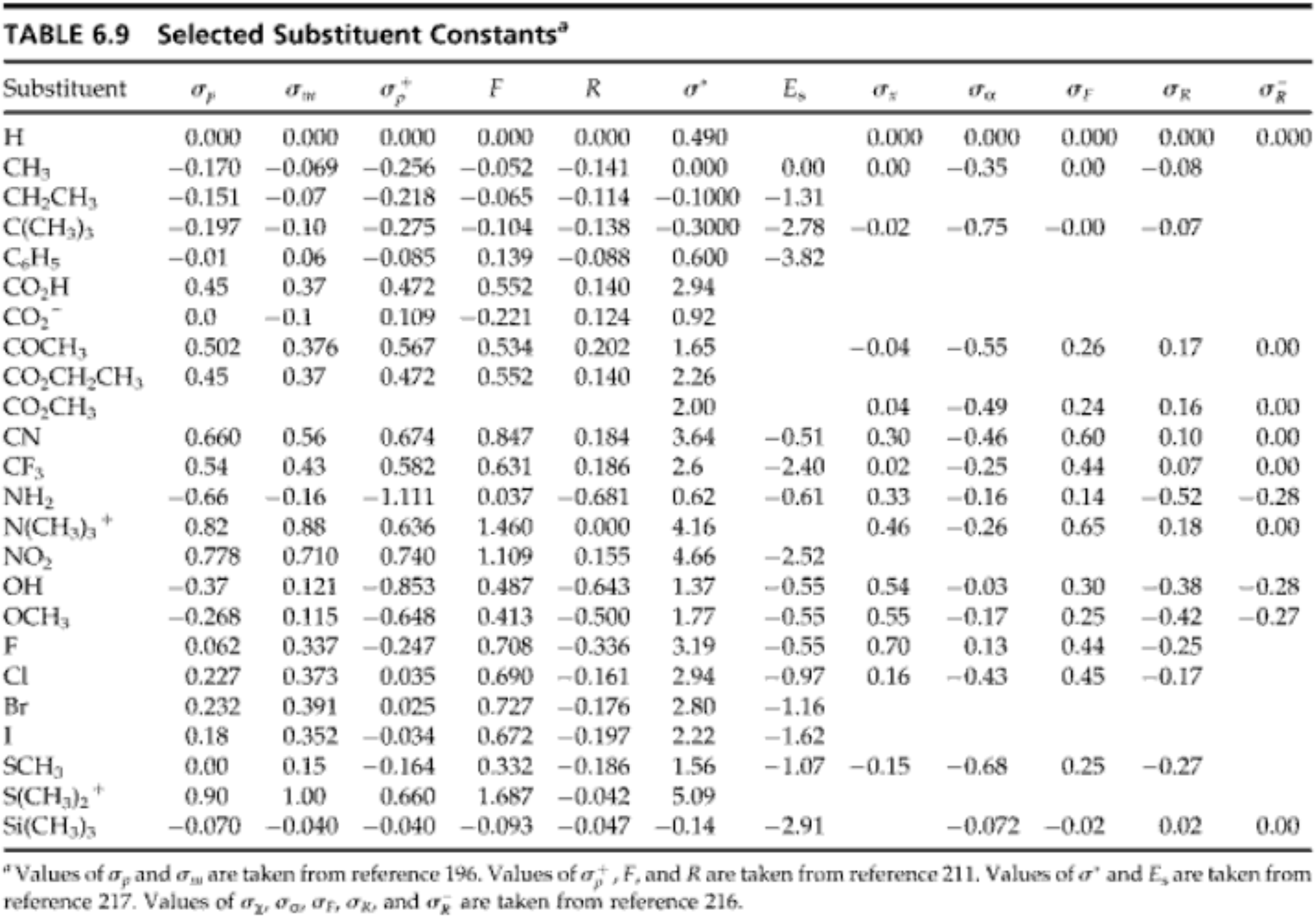
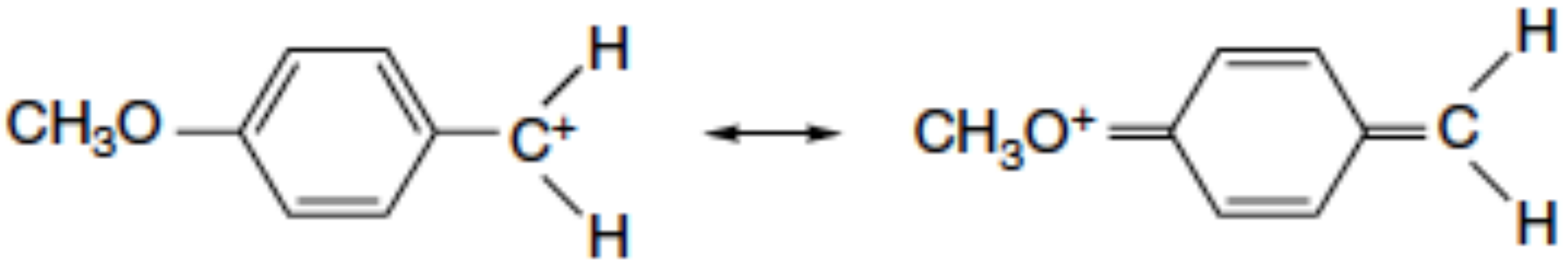


TABLE 6.9 Selected Substituent Constants[a]

Substituent	σ_p	σ_m	σ_p^+	F	R	σ^*	E_s	σ_χ	σ_α	σ_F	σ_R	σ_R^-
H	0.000	0.000	0.000	0.000	0.000	0.490		0.000	0.000	0.000	0.000	0.000
CH_3	−0.170	−0.069	−0.256	−0.052	−0.141	0.000	0.00	0.00	−0.35	0.00	−0.08	
CH_2CH_3	−0.151	−0.07	−0.218	−0.065	−0.114	−0.1000	−1.31					
$C(CH_3)_3$	−0.197	−0.10	−0.275	−0.104	−0.138	−0.3000	−2.78	−0.02	−0.75	−0.00	−0.07	
C_6H_5	−0.01	0.06	−0.085	0.139	−0.088	0.600	−3.82					
CO_2H	0.45	0.37	0.472	0.552	0.140	2.94						
CO_2^-	0.0	−0.1	0.109	−0.221	0.124	0.92						
$COCH_3$	0.502	0.376	0.567	0.534	0.202	1.65		−0.04	−0.55	0.26	0.17	0.00
$CO_2CH_2CH_3$	0.45	0.37	0.472	0.552	0.140	2.26						
CO_2CH_3						2.00		0.04	−0.49	0.24	0.16	0.00
CN	0.660	0.56	0.674	0.847	0.184	3.64	−0.51	0.30	−0.46	0.60	0.10	0.00
CF_3	0.54	0.43	0.582	0.631	0.186	2.6	−2.40	0.02	−0.25	0.44	0.07	0.00
NH_2	−0.66	−0.16	−1.111	0.037	−0.681	0.62	−0.61	0.33	−0.16	0.14	−0.52	−0.28
$N(CH_3)_3^+$	0.82	0.88	0.636	1.460	0.000	4.16		0.46	−0.26	0.65	0.18	0.00
NO_2	0.778	0.710	0.740	1.109	0.155	4.66	−2.52					
OH	−0.37	0.121	−0.853	0.487	−0.643	1.37	−0.55	0.54	−0.03	0.30	−0.38	−0.28
OCH_3	−0.268	0.115	−0.648	0.413	−0.500	1.77	−0.55	0.55	−0.17	0.25	−0.42	−0.27
F	0.062	0.337	−0.247	0.708	−0.336	3.19	−0.55	0.70	0.13	0.44	−0.25	
Cl	0.227	0.373	0.035	0.690	−0.161	2.94	−0.97	0.16	−0.43	0.45	−0.17	
Br	0.232	0.391	0.025	0.727	−0.176	2.80	−1.16					
I	0.18	0.352	−0.034	0.672	−0.197	2.22	−1.62					
SCH_3	0.00	0.15	−0.164	0.332	−0.186	1.56	−1.07	−0.15	−0.68	0.25	−0.27	
$S(CH_3)_2^+$	0.90	1.00	0.660	1.687	−0.042	5.09						
$Si(CH_3)_3$	−0.070	−0.040	−0.040	−0.093	−0.047	−0.14	−2.91		−0.072	−0.02	0.02	0.00

[a] Values of σ_p and σ_m are taken from reference 196. Values of σ_p^+, F, and R are taken from reference 211. Values of σ^* and E_s are taken from reference 217. Values of σ_χ, σ_α, σ_F, σ_R, and σ_R^- are taken from reference 216.

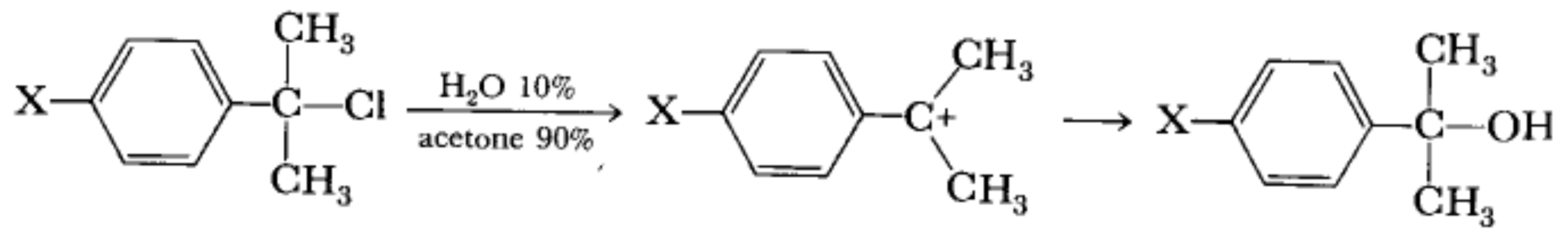
Conjugação Direta: Hammett dá falhas

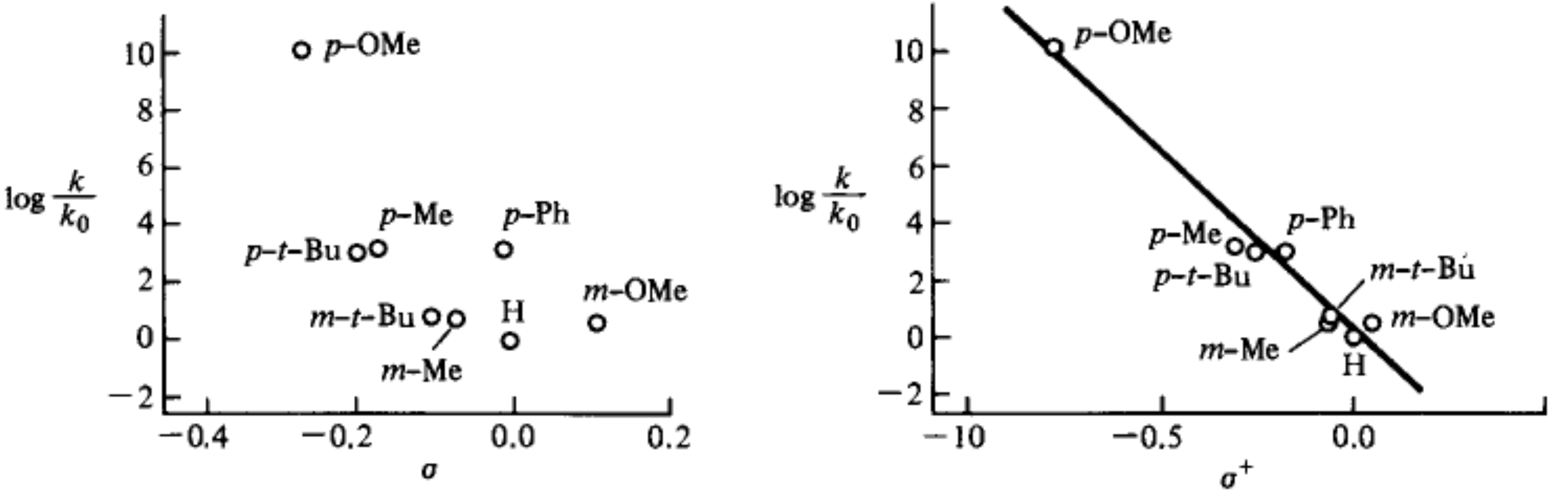


Direct resonance interaction with cationic center

Direct resonance interaction with anionic center

Falhas para σ: Uso de σ^+

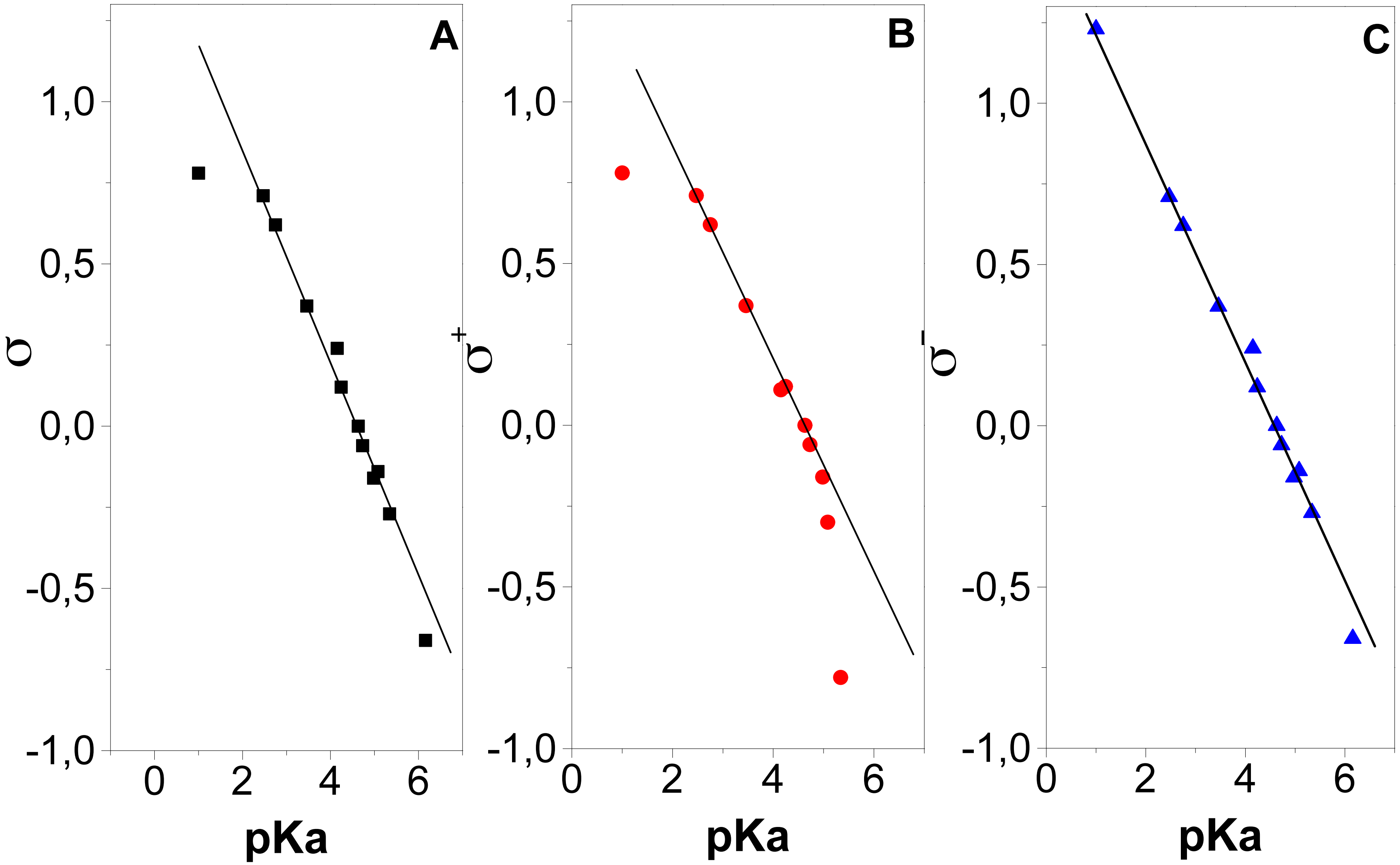




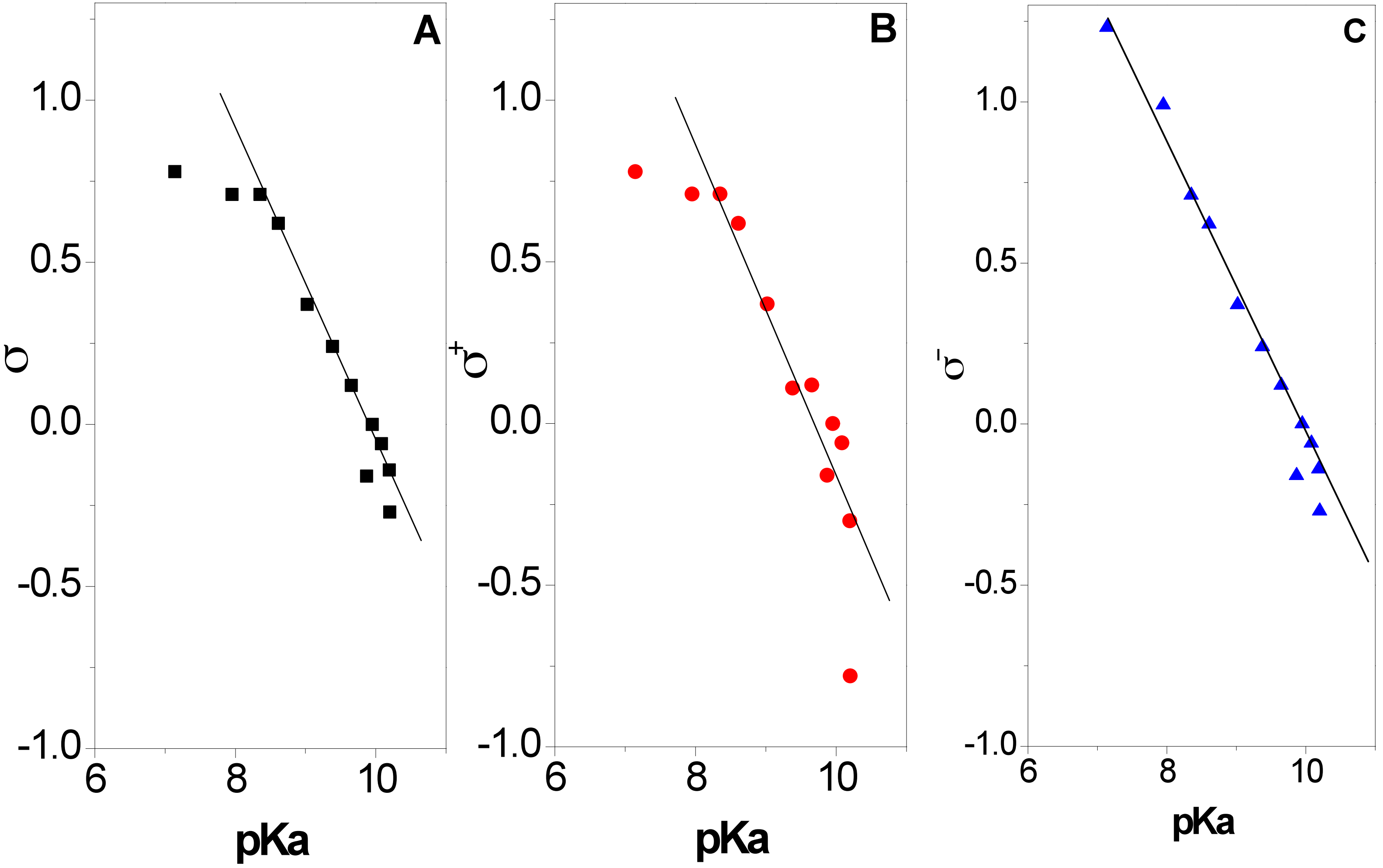
(a) (b)

Figure 2.7 Bromination of monosubstituted benzenes in acetic acid. In (a) data are plotted against σ; in (b) against σ^+. Reprinted with permission from Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958,** *80*, 4979. Copyright 1958 American Chemical Society.

Anilina



Fenol



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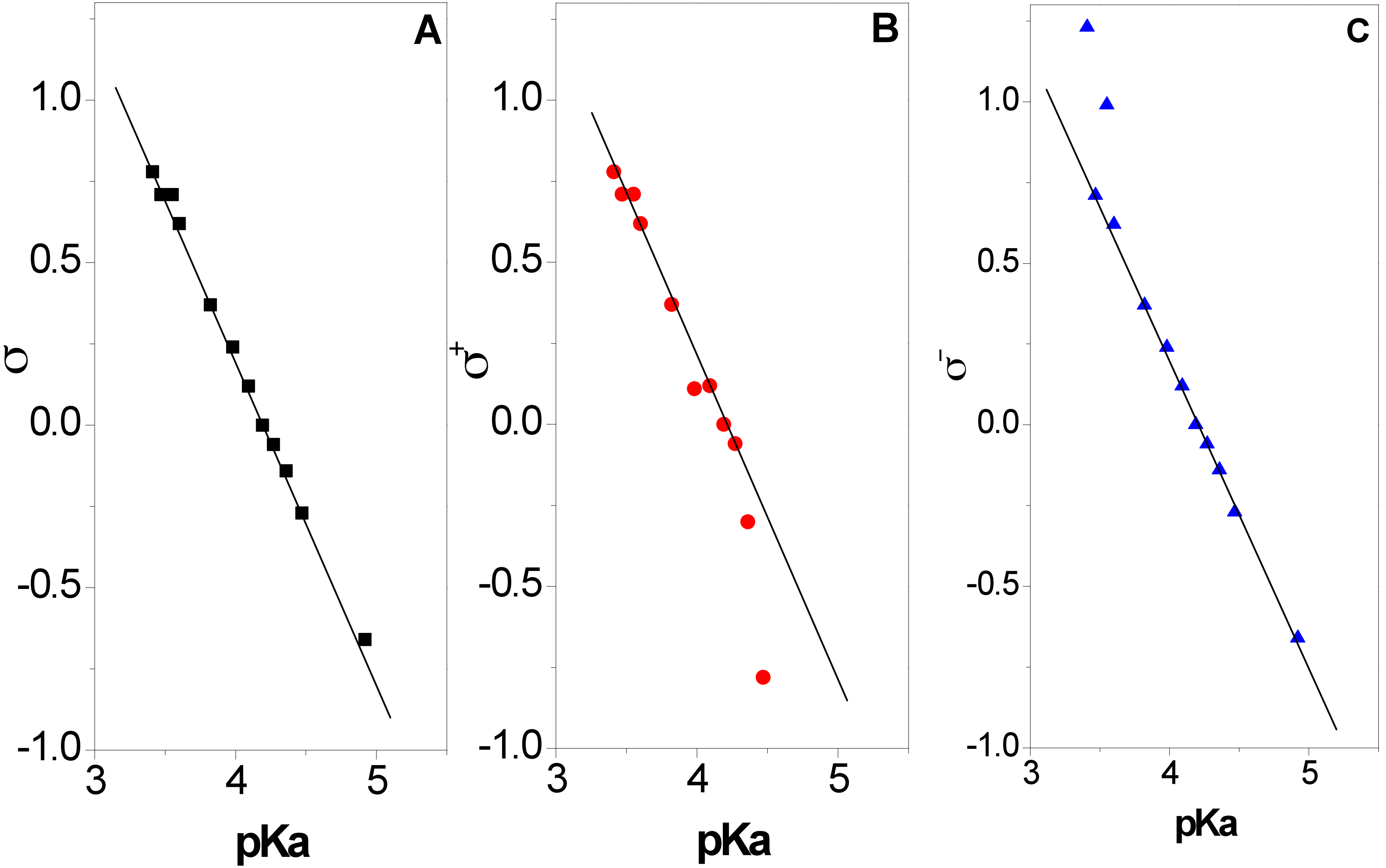


Equações de Brown-Okamoto

Para ressonância direta (através do anel) entre G e o centro da reação:

1- Carga *positiva* no centro reacional, está sendo estabilizada pelo substituinte G (*doador de elétrons*):

$$\text{Log } (k_{\mathbf{G}} \text{ ou } K_{\mathbf{G}} / k_{\mathbf{H}} \text{ ou } K_{\mathbf{H}}) = \rho^{+}{}_{\textbf{(Reação ou equilíbrio)}} \sigma^{+}{}_{\mathbf{G}}$$

2- Carga *negativa* no centro reacional, está sendo estabilizada pelo substituinte G (*aceitador de elétrons*):

$$\text{Log } (k_{\mathbf{G}} \text{ ou } K_{\mathbf{G}} / k_{\mathbf{H}} \text{ ou } K_{\mathbf{H}}) = \rho^{-}{}_{\textbf{(Reação ou equilíbrio)}} \sigma^{-}{}_{\mathbf{G}}$$

3- Casos “intermediários” , Equação de Yukawa-Tsuno

$$\text{Log } (k_{\mathbf{G}} \text{ ou } K_{\mathbf{G}} / k_{\mathbf{H}} \text{ ou } K_{\mathbf{H}}) =$$

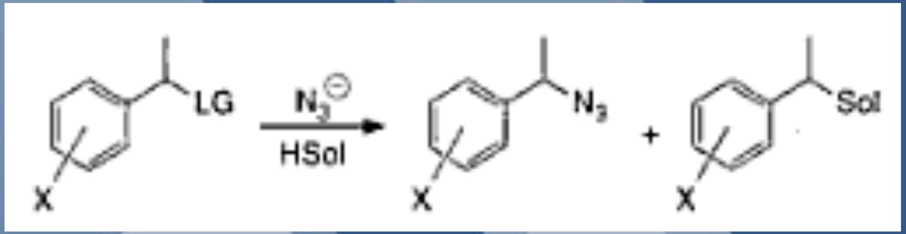
$$\rho(\sigma + r\ (\sigma^{+}{}_{\mathbf{G}} \text{ ou } \sigma^{-}{}_{\mathbf{G}} - \sigma)$$

Onde r = grau de participação da ressonância direta do grupo G com o centro da reação.

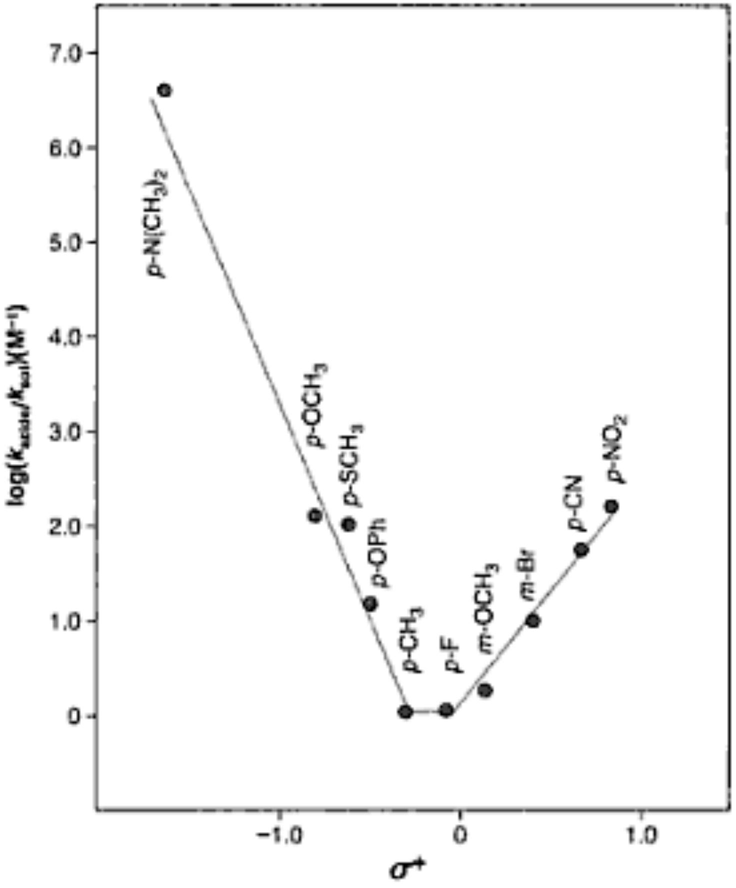
Para r = 0, não há ressonância direta → Eq. de Hammett,

Para r = 1, a ressonância é direta → Brown-Okamoto

Desvios da Linearidade em Hammett

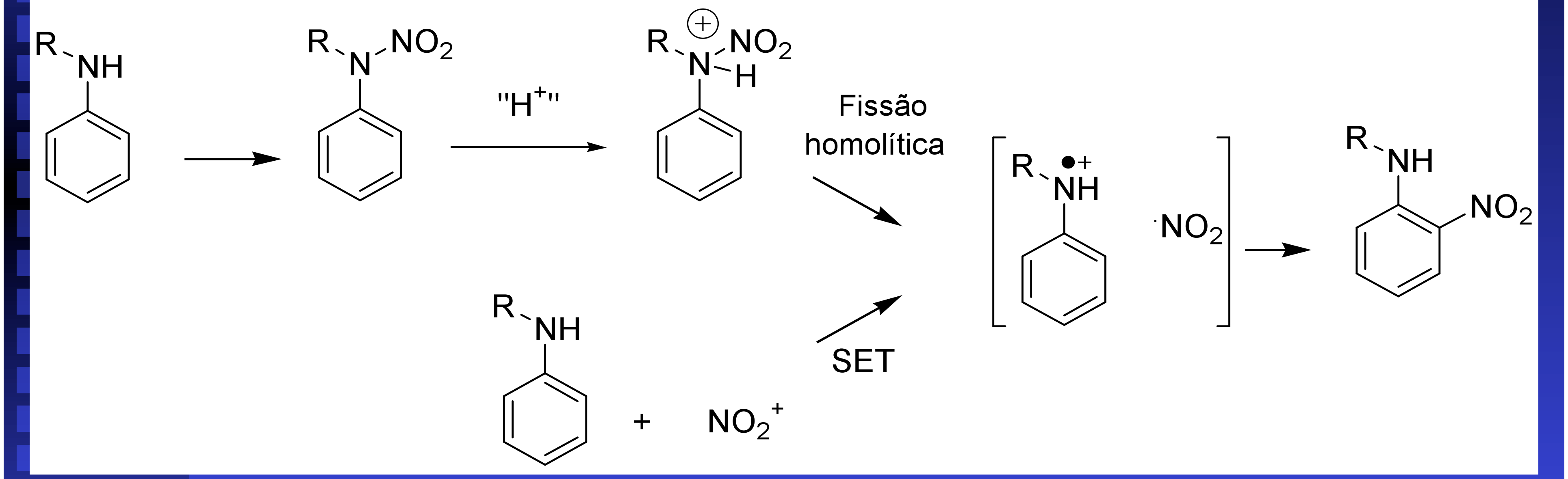


- Mudança de S_N1 para S_N2

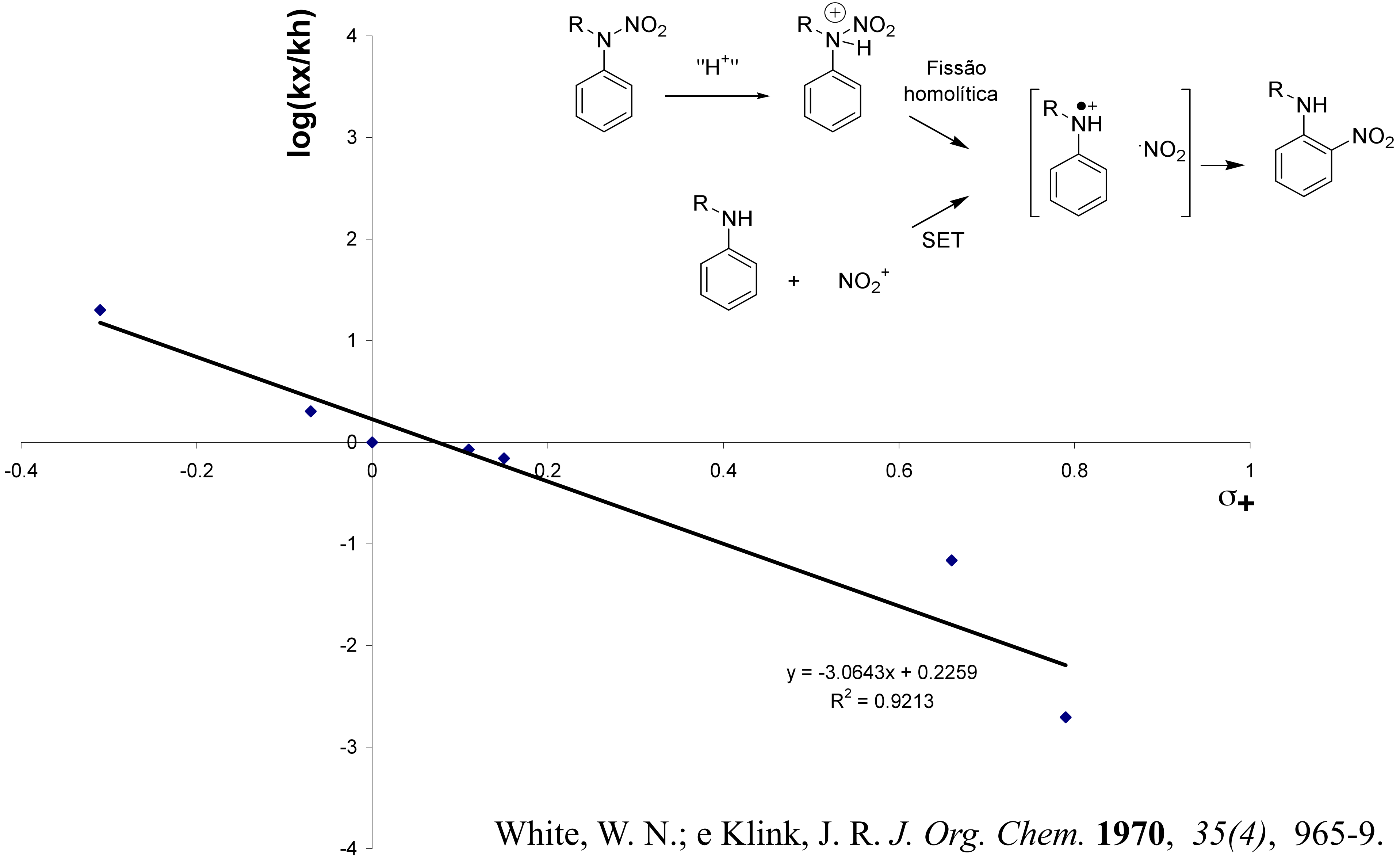


Richard, J. P., and Jencks, W. P. "A Simple Relationship between Carbocation Lifetime and Reactivity–Selectivity Relationships for the Solvolysis of Ring-Substituted 1-Phenylethyl Derivatives." *J. Am. Chem. Soc.*, **104**, 4689–4691 (1982).

Rearrangement of N-Nitroanilines

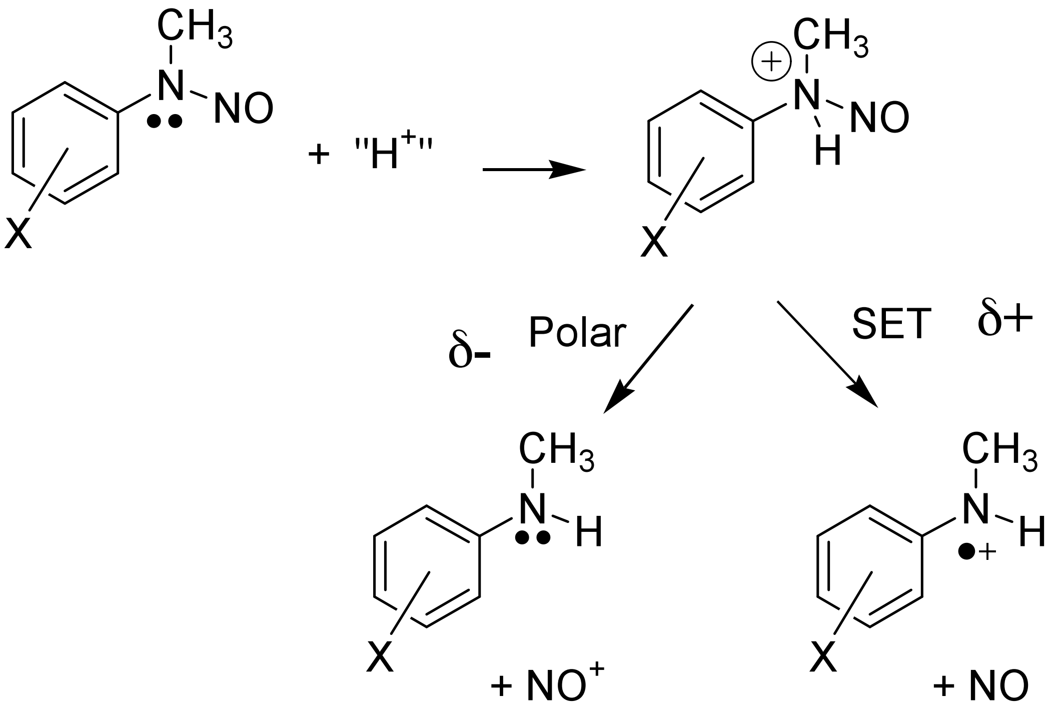


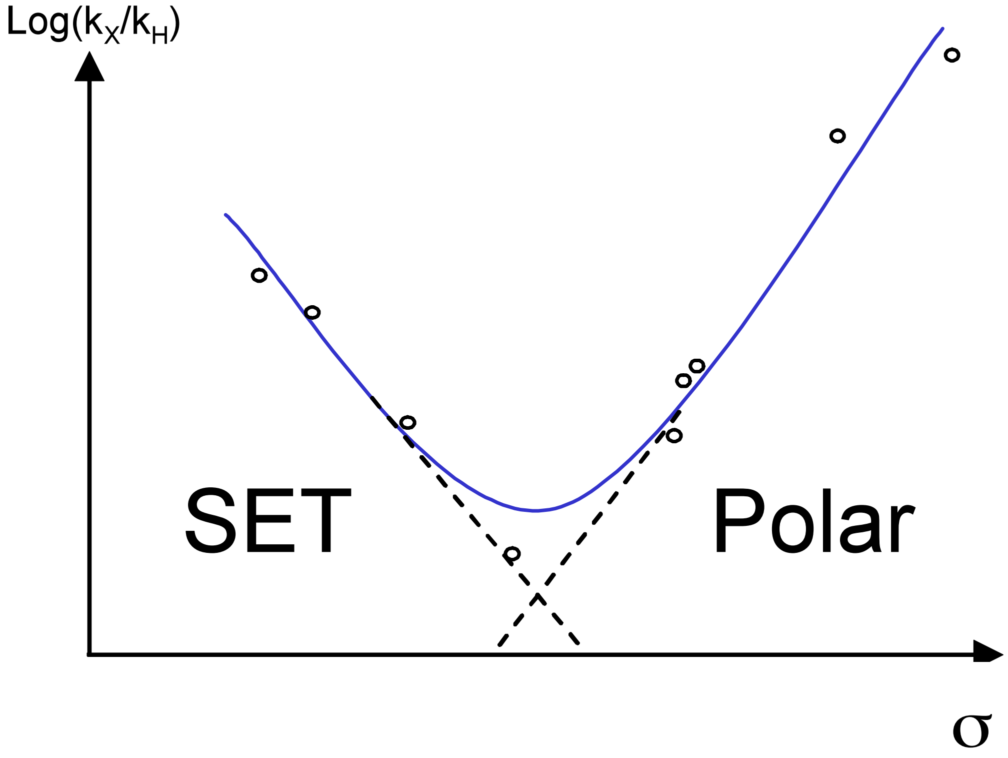
Hammett correlation



White, W. N.; e Klink, J. R. *J. Org. Chem.* **1970**, *35(4)*, 965-9.

Rearrangement of N-Nitrosoanilines

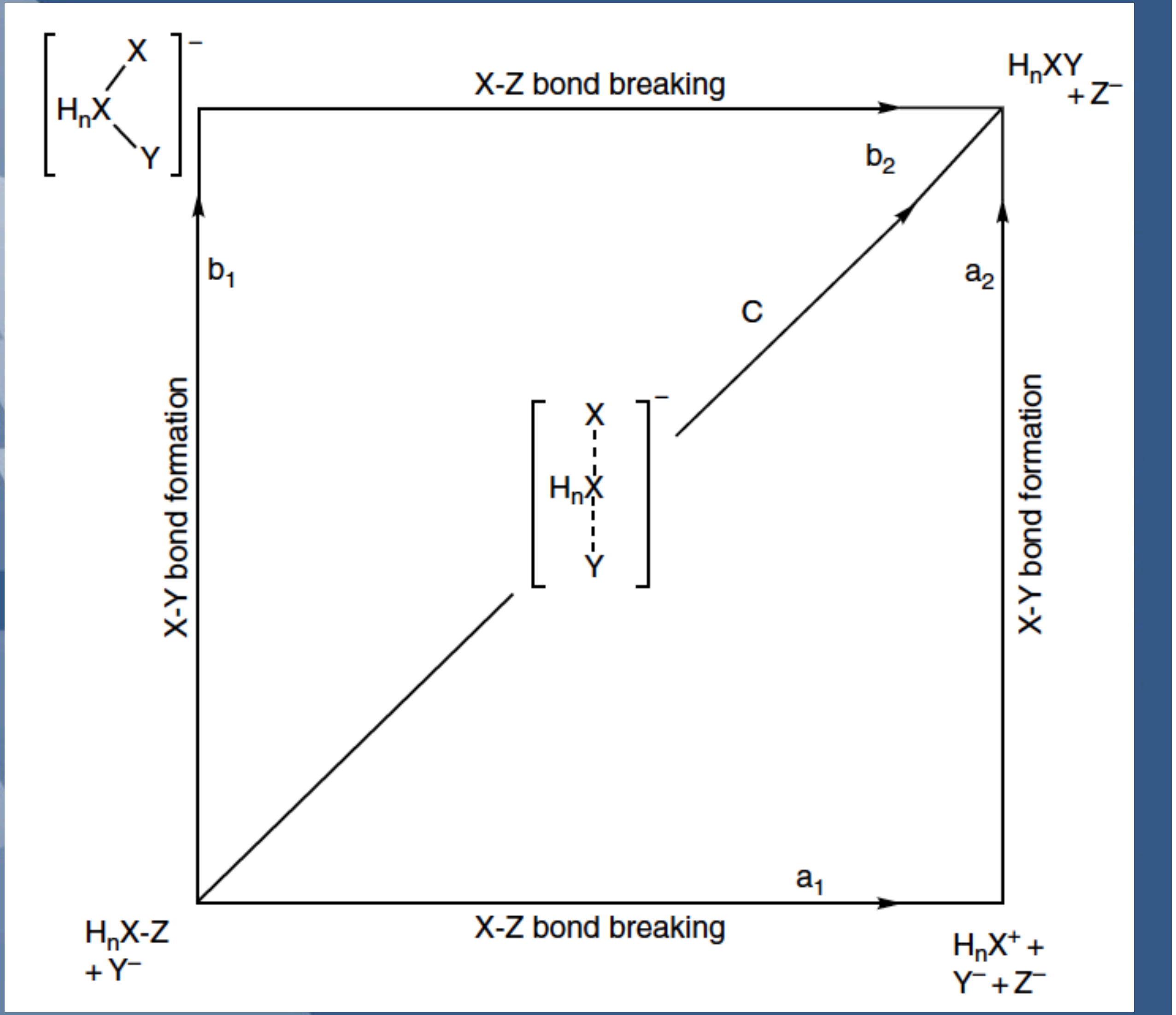




Diagramas de Albery-More O'Ferrall-Jencks

R. A. More O'Ferrall

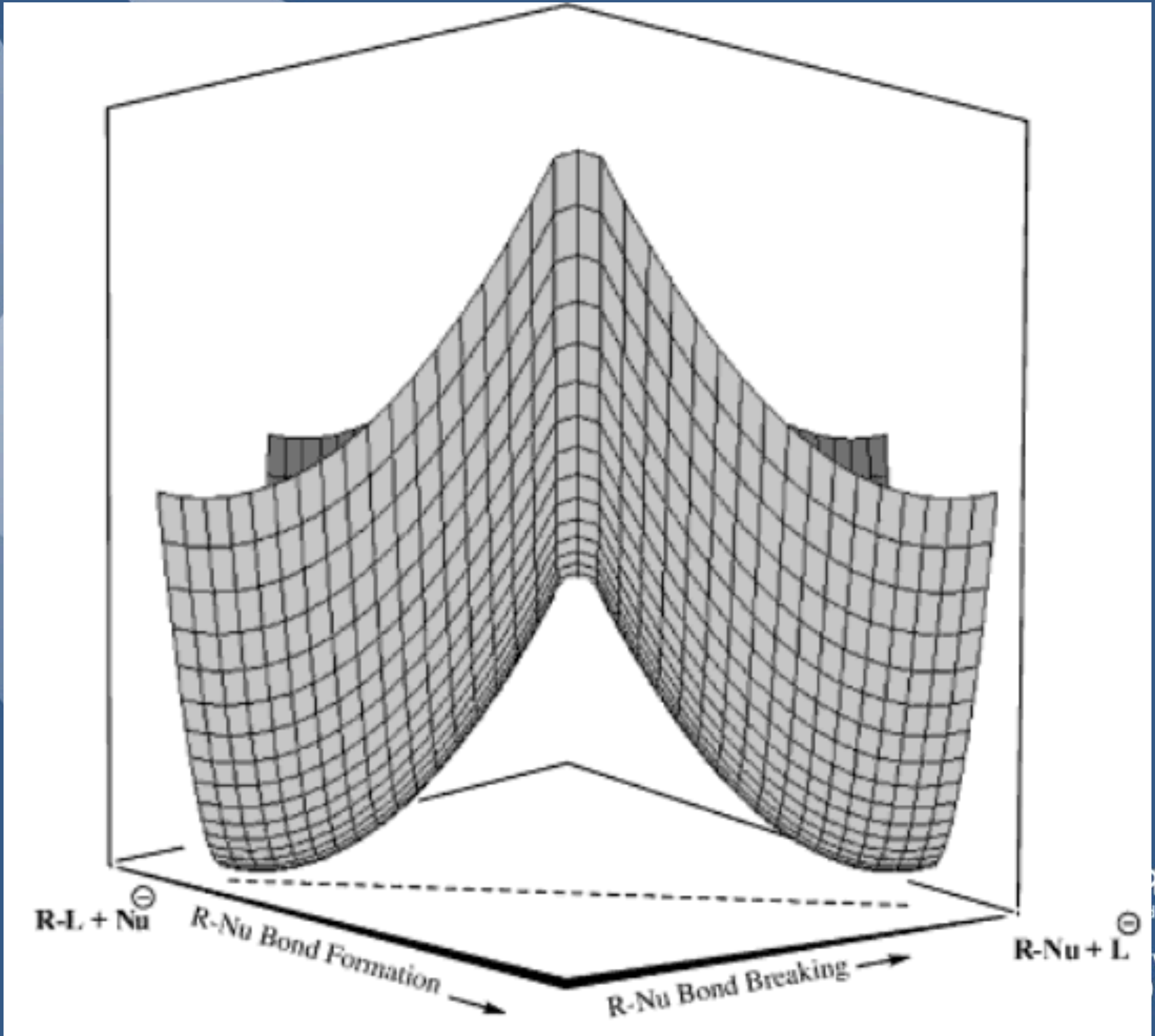
William P. Jencks



W. J. Albery, *Prog. React. Kinetics*, ***4, 353 (1967);***

R. A. More O'Ferrall, J. Chem. Soc. B, 274 (1970);

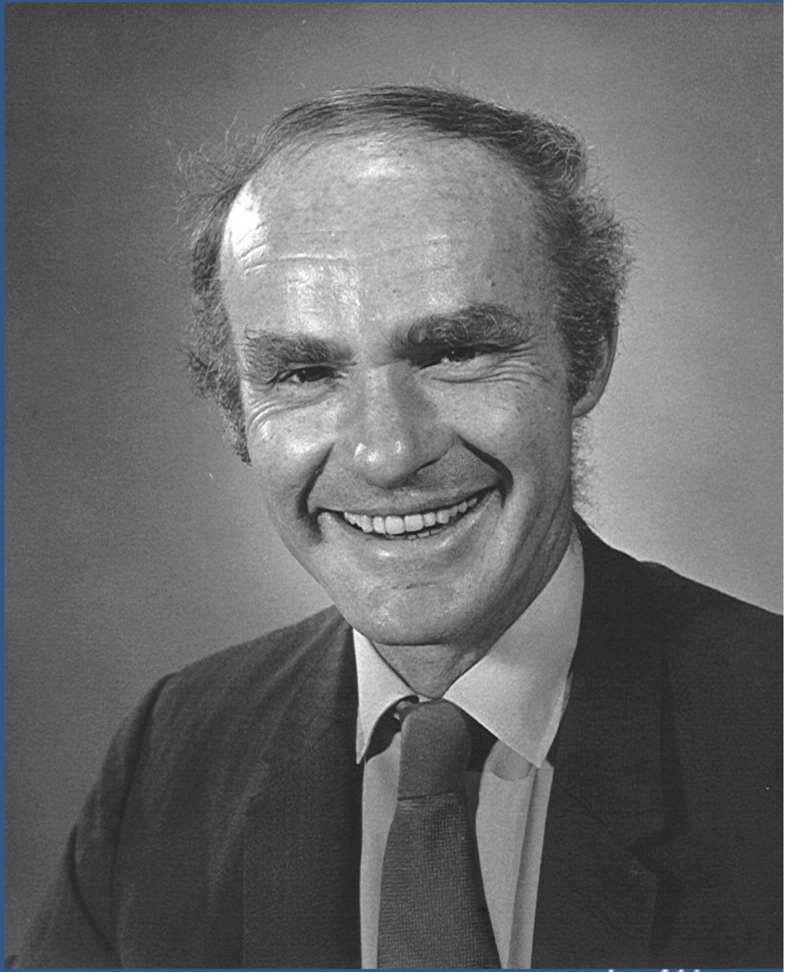
W. P. Jencks, *Chem. Rev.*, ***72, 705 (1972).***


R-L + Nu⊖
R-Nu Bond Formation →
R-Nu Bond Breaking →
R-Nu + L⊖

Postulado de Hammond

"If two states, as, for example, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small reorganization of molecular structure."

G. S. Hammond, *J. Am. Chem. Soc.*, ***77, 334 (1955)***



George Simms Hammond (1921 - 2005)

“If two states, as, for example, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small reorganization of molecular structure.”

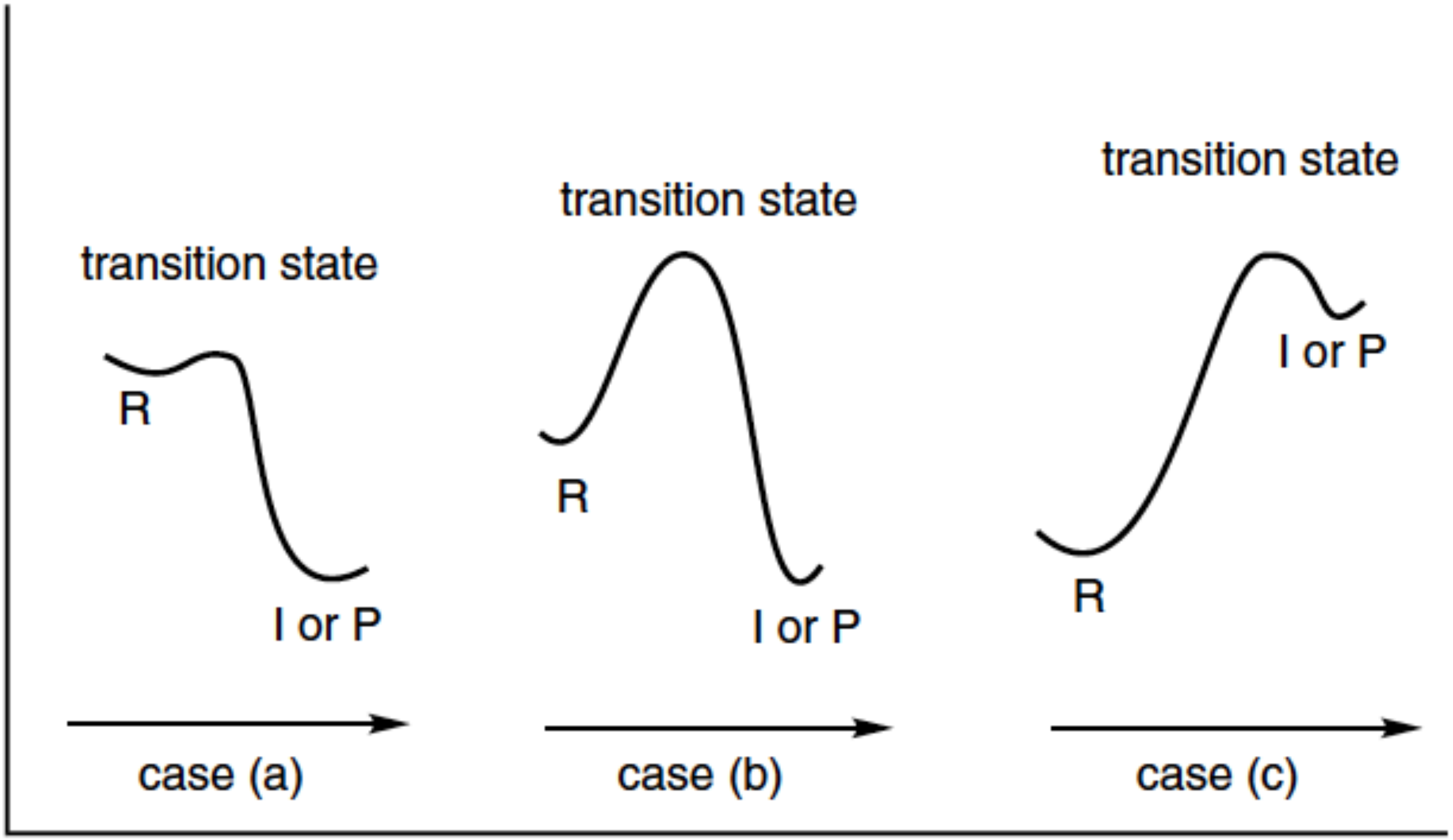


Fig. 3.11. Reaction energy diagram illustrating Hammond’s postulate: (a) early transition structure resembles reactant, (b) midpoint transition structure resembles neither reactant or product, (c) late transition structure resembles intermediate or product.

Gráfico da E_a x ΔH

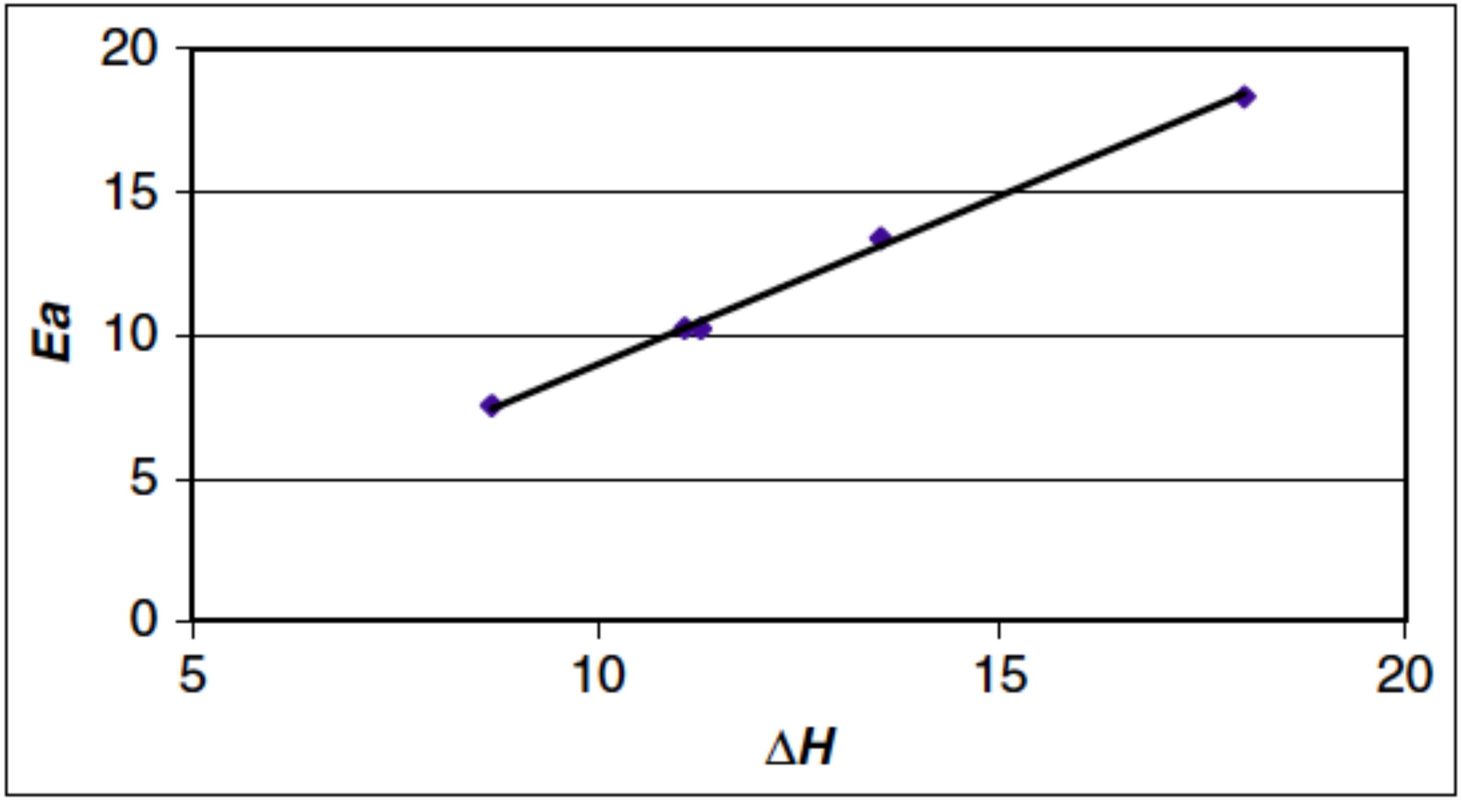


Fig. 3.10. Plot of E_a for abstraction of hydrogen from alkanes by bromine atom versus ΔH.

Fatores que alteram a acidez e a basicidade: efeitos da estrutura e do solvente

3

Acidez e basicidade são conceitos termodinâmicos

- Acidez/basicidade são regidos pela equação de Gibbs
- $\Delta G^o = \Delta H^o - T\Delta S^o$

ΔH^o = estabilidade, “conforto molecular”

ΔS^o = liberdade

O pK_a correlaciona-se linearmente com o ΔG^o

$$HA + H_2O \rightarrow A^- + H_3O^+$$

$$K_{eq} = \frac{[A^-][H_3O^+]}{[HA][H_2O]}$$

$$K_{eq}[H_2O] = \frac{[A^-][H_3O^+]}{[HA]} \approx cte = K_a$$

$$pK_a = -\log K_a$$

$$pK_a = -\log (K_{eq.}[H_2O])$$

O pK_a correlaciona-se linearmente com o ΔGº

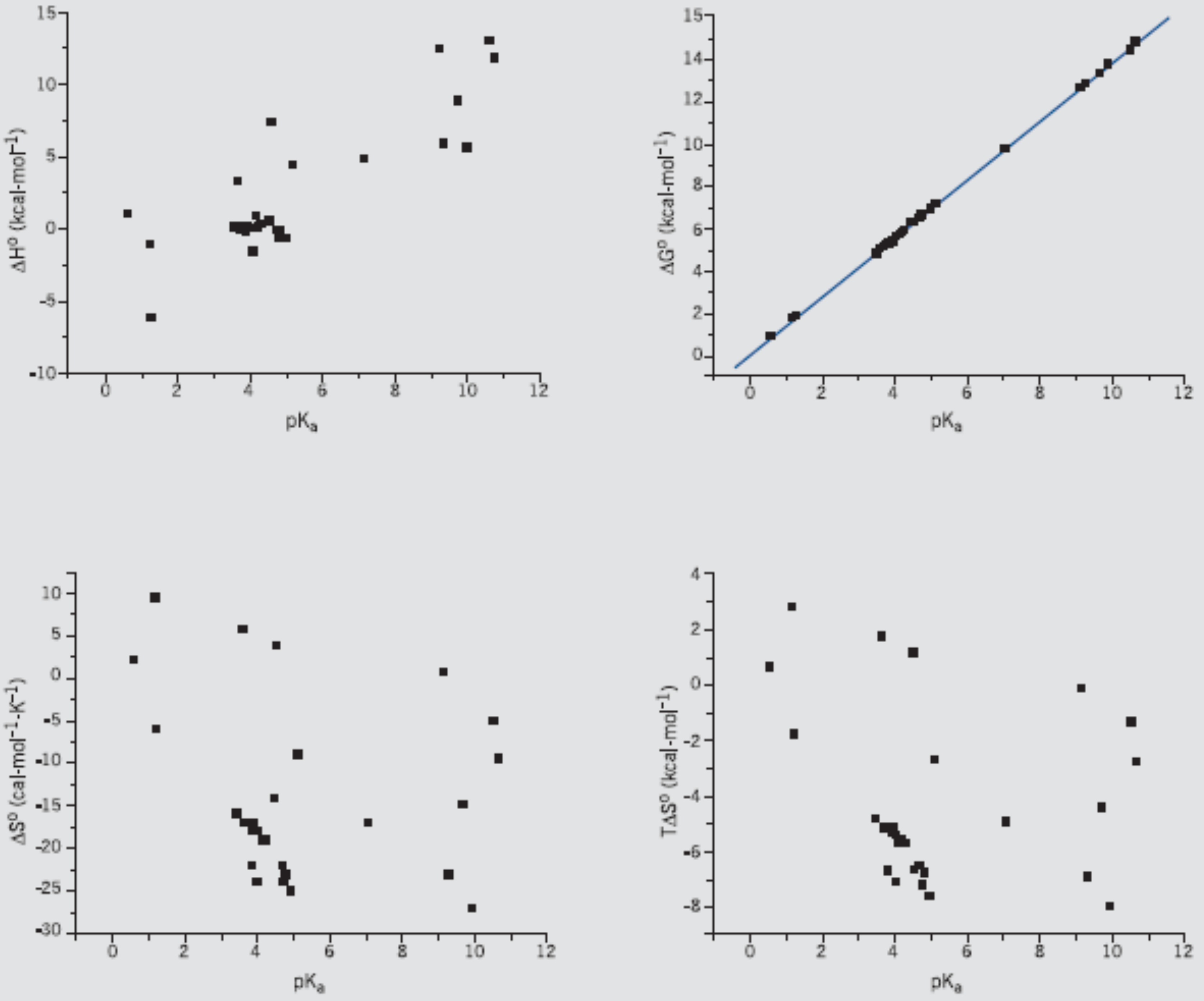
$$pK_a = -\log K_{eq.} - \log[H_2O]$$

$$-\log K_{eq.} = pK_a + \log[H_2O]$$

$$\Delta G^o = -RT \ln K_{eq} = 2{,}303\ RT\ (-\log K_{eq})$$

$$\Delta G^o = 2{,}303\ RT\ (pK_a + \log[H_2O])$$

$$\Delta G^o = 1{,}4\ pK_a + 2{,}34\ (T = 298\ K)$$



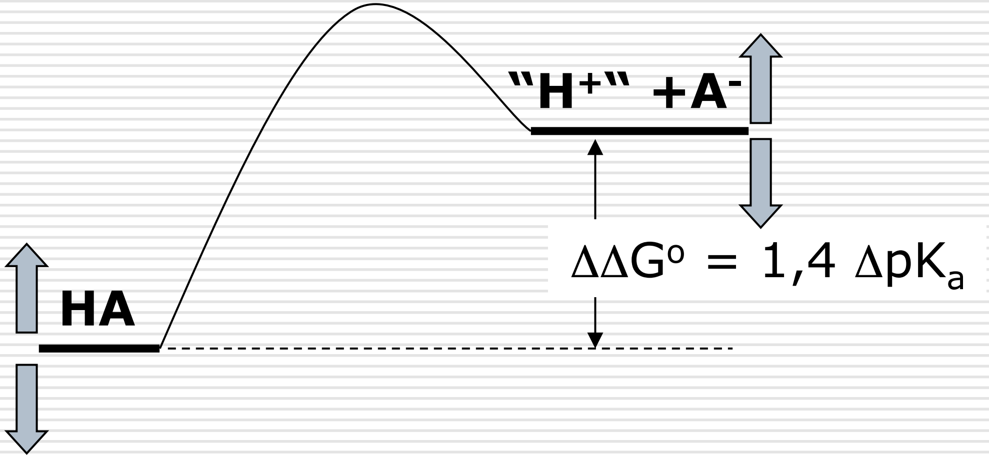
ΔH^o (kcal-mol^{-1})
15
10
5
0
-5
-10
0
2
4
6
8
10
12
pK$_a$
ΔG^o (kcal-mol^{-1})
15
14
12
10
8
6
4
2
0
0
2
4
6
8
10
12
pK$_a$
ΔS^o (cal-mol^{-1}-K^{-1})
10
5
0
-5
-10
-15
-20
-25
-30
0
2
4
6
8
10
12
pK$_a$
$T\Delta S^o$ (kcal-mol^{-1})
4
2
0
-2
-4
-6
-8
0
2
4
6
8
10
12
pK$_a$

Tudo o que afeta ΔGº deverá afetar posição do equilíbrio

- ☐ Estabilidade dos reagentes
- ☐ Estabilidade do produto
- ☐ Solvatação nos reagentes e nos produtos

Propriedade Intríseca

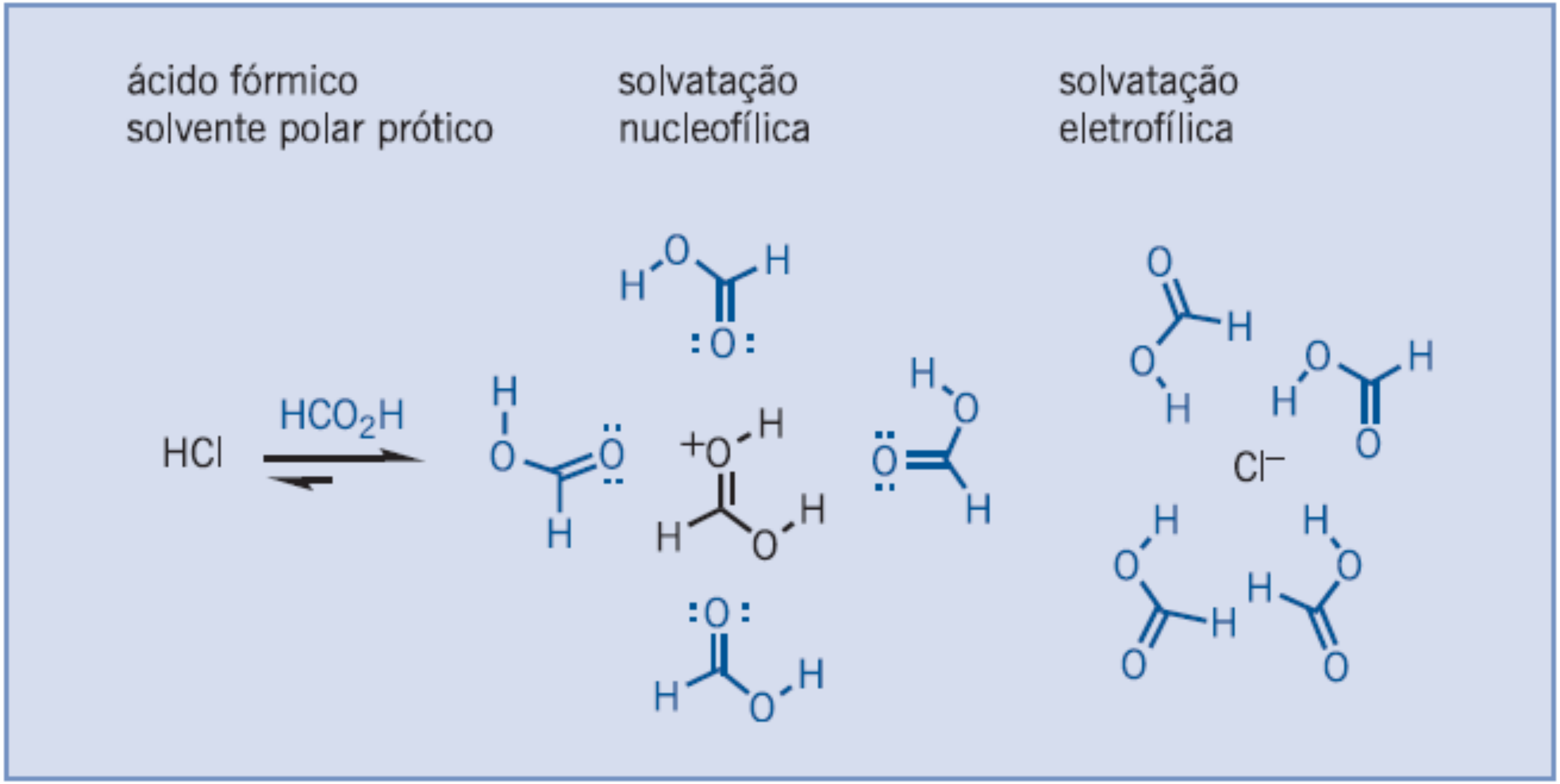
Depende do meio



$\Delta\Delta G^o = 1{,}4\ \Delta pK_a$

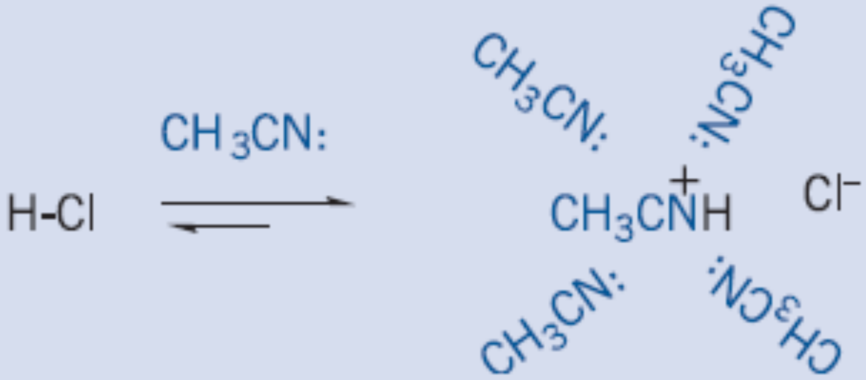
Estrutura Molecular
&
Solvatação

Solvatação Eletrofílica

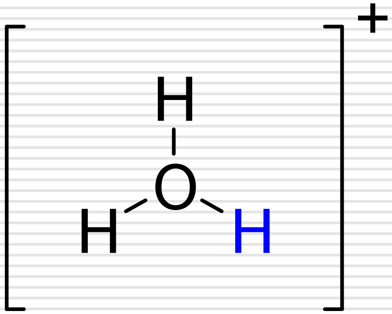


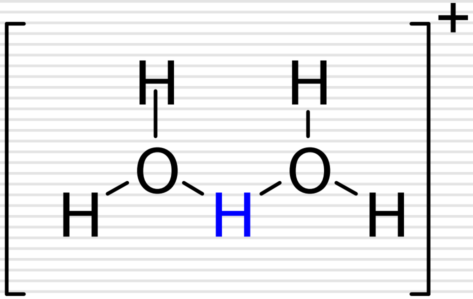
Solvatação Nucleofílica

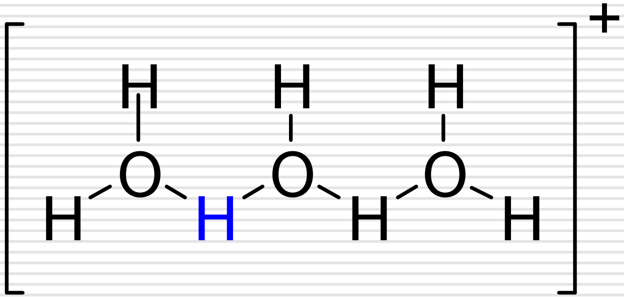
acetonitrila
solvente polar aprótico

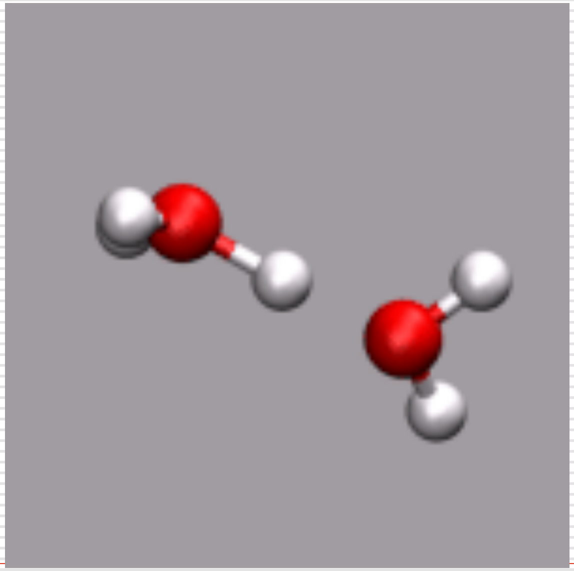


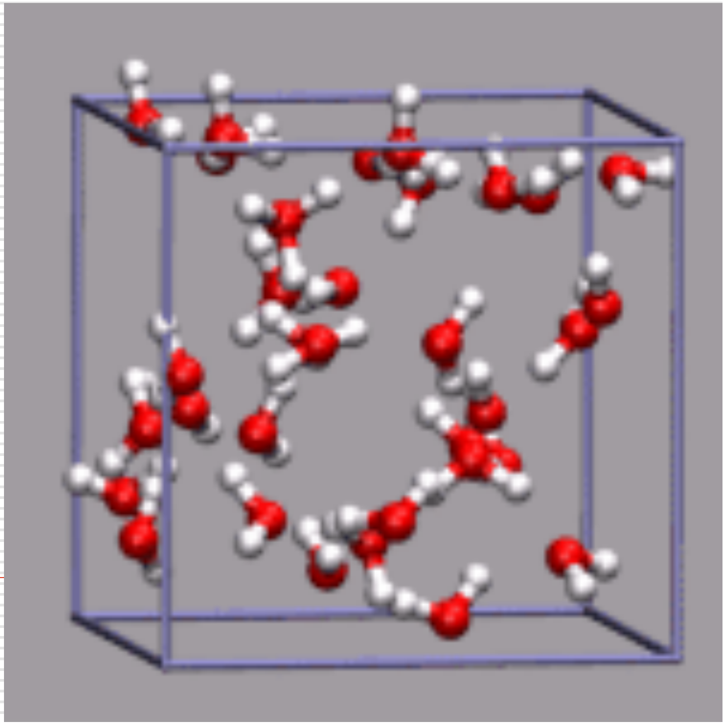
Solvatação Nucleofílica do H_3O^+











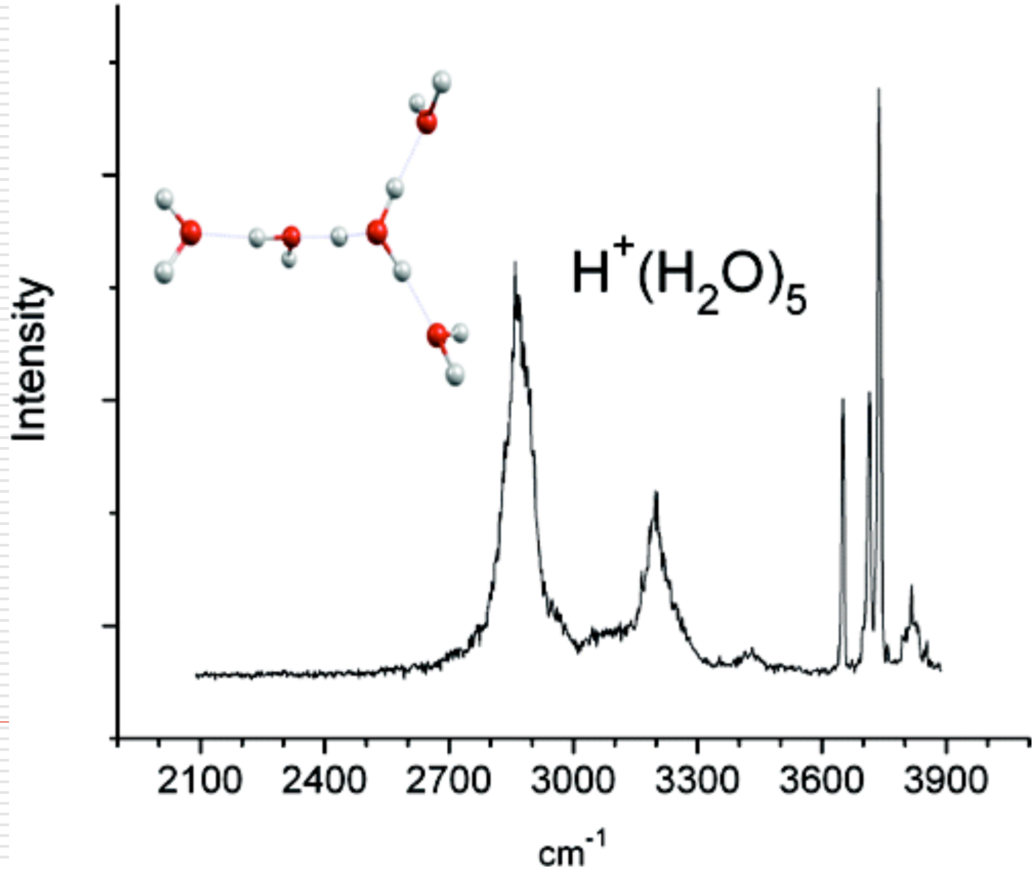
4570 *J. Phys. Chem. A* **2010,** *114,* 4570–4579

Infrared Spectroscopy of Small Protonated Water Clusters, $H^+(H_2O)_n$ ($n = 2-5$): Isomers, Argon Tagging, and Deuteration

G. E. Douberly,[†] R. S. Walters,[†] J. Cui,[‡] K. D. Jordan,[‡] and M. A. Duncan*[,†]

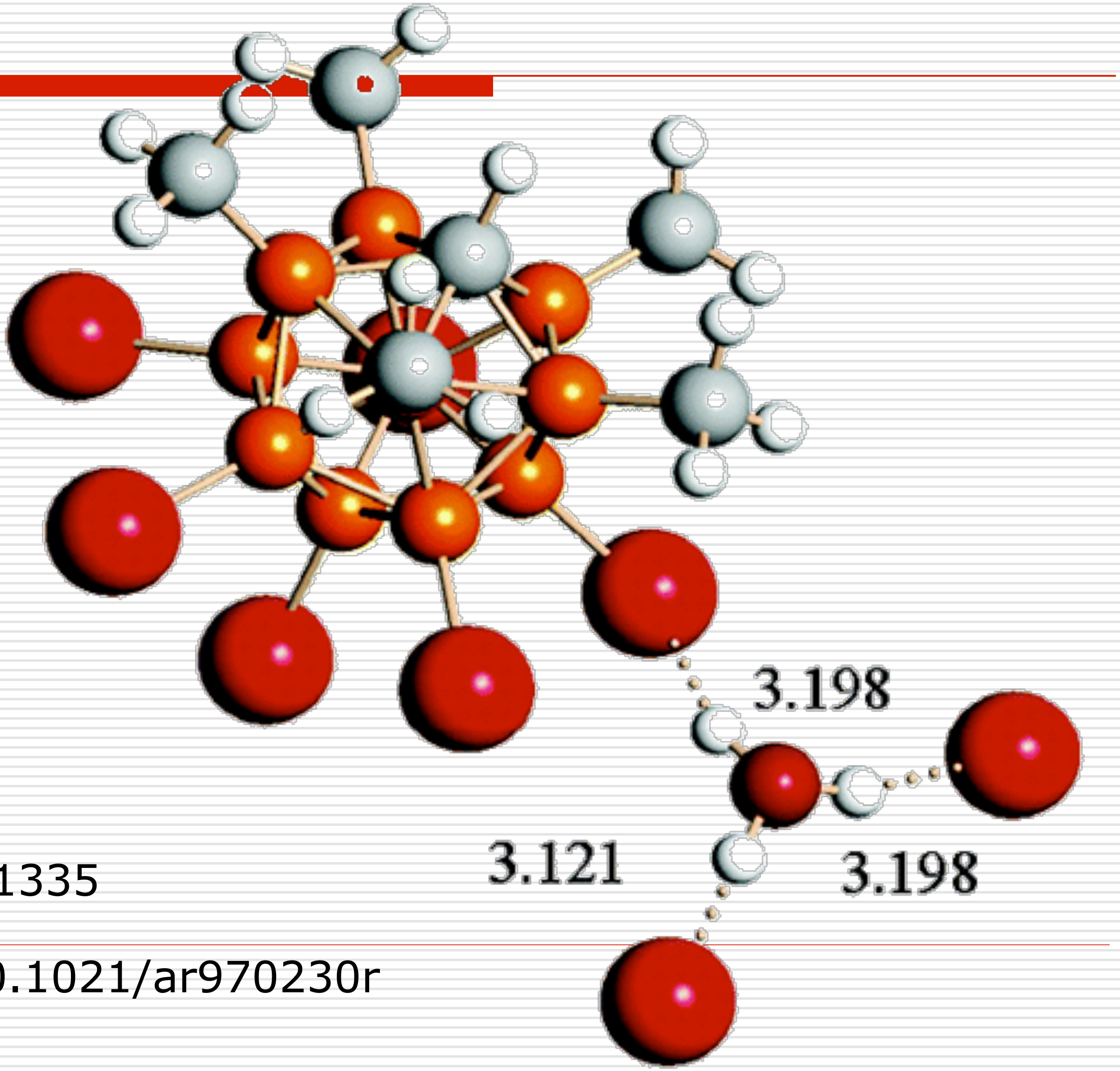
Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556, and Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, Pennsylvania 15260

Received: January 26, 2010; Revised Manuscript Received: March 1, 2010



DOI: 10.1021/jp100778s

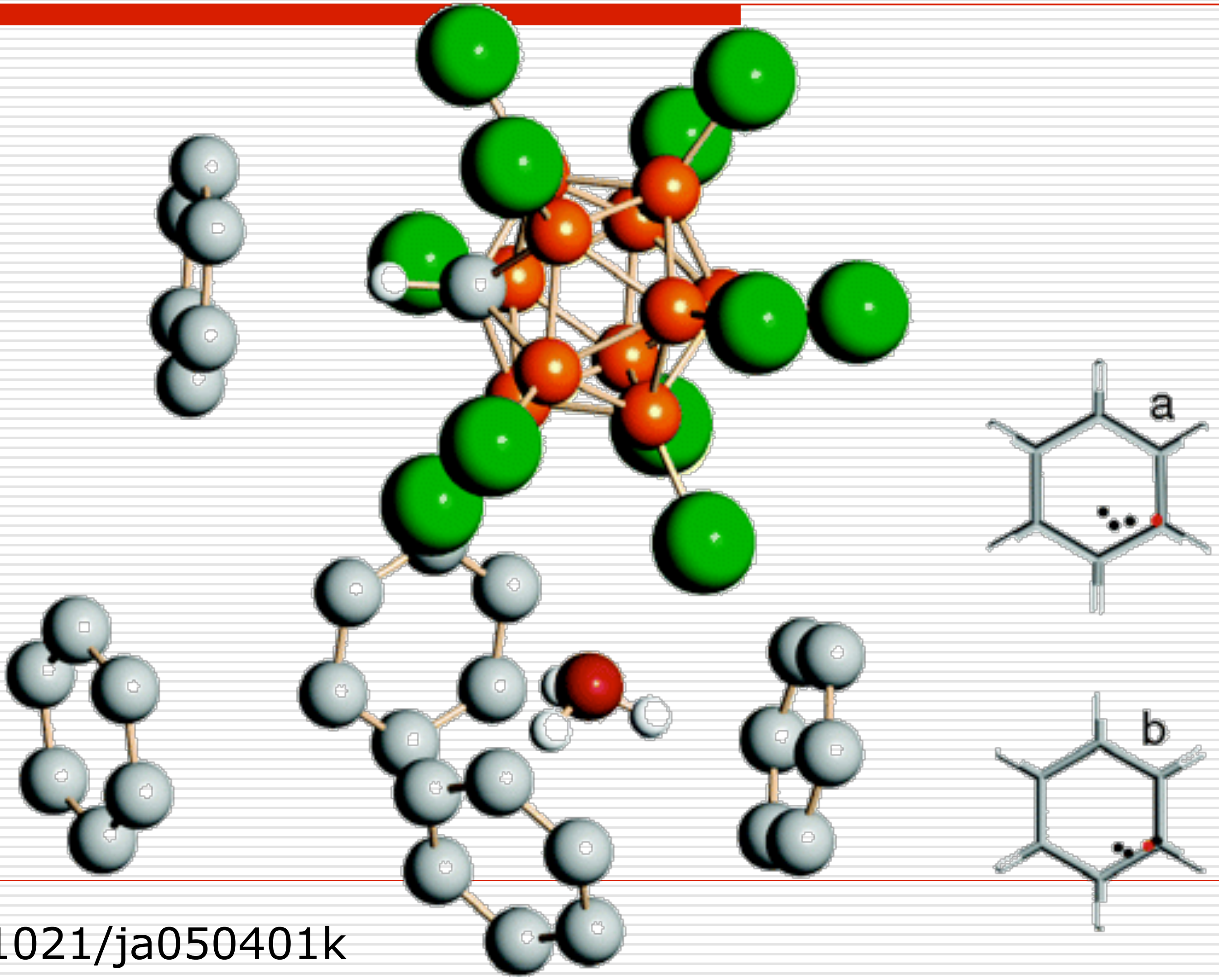
Estrutura do $H_3O^+\{CHB_{11}Me_5Br_6\}^-$



DOI: 10.1021/ja0551335

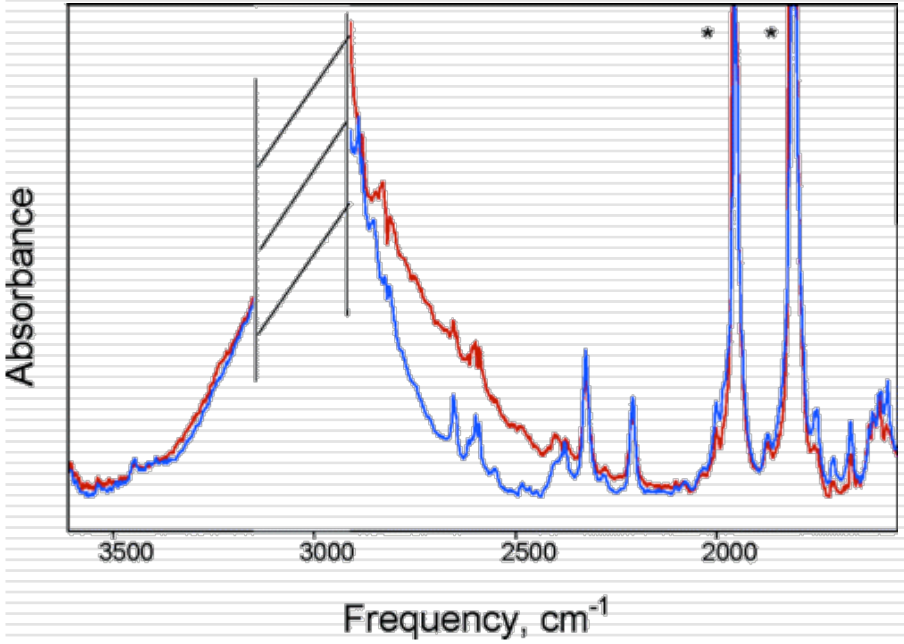
Carboranas: DOI: 10.1021/ar970230r

Estrutura (raios-X) do $[H_3O \cdot 3C_6H_6][CHB_{11}Cl_{11}] \cdot C_6H_6$

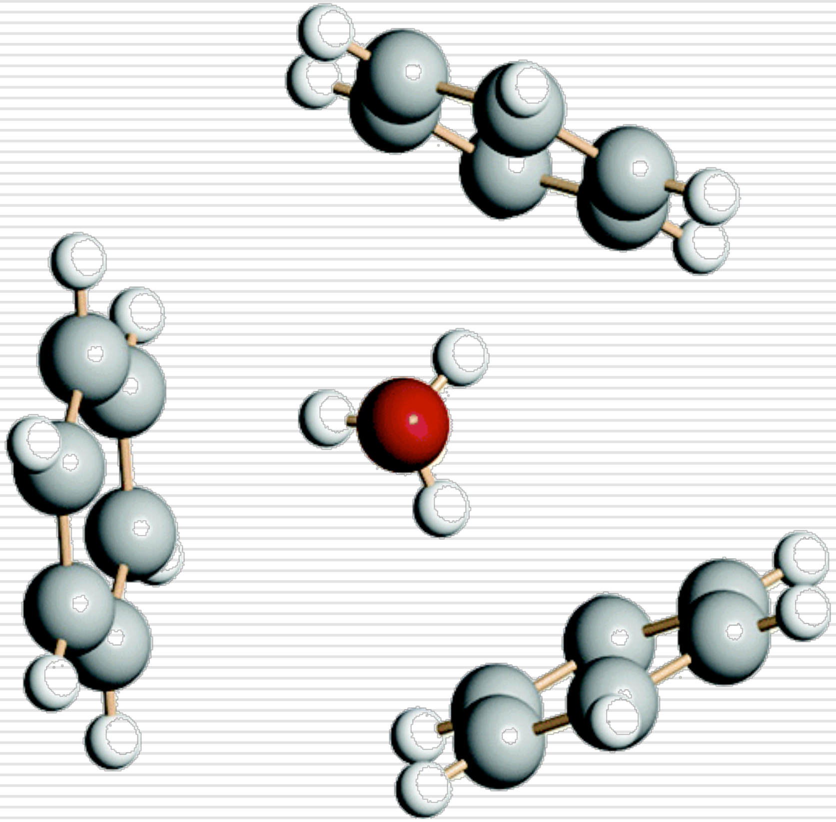


DOI: 10.1021/ja050401k

Estrutura do $H_3O^+ \cdot 3PhH$ na estrutura de raios-X do sal $CHB_{11}Cl_{11}^-$



DOI: 10.1021/ja0551335



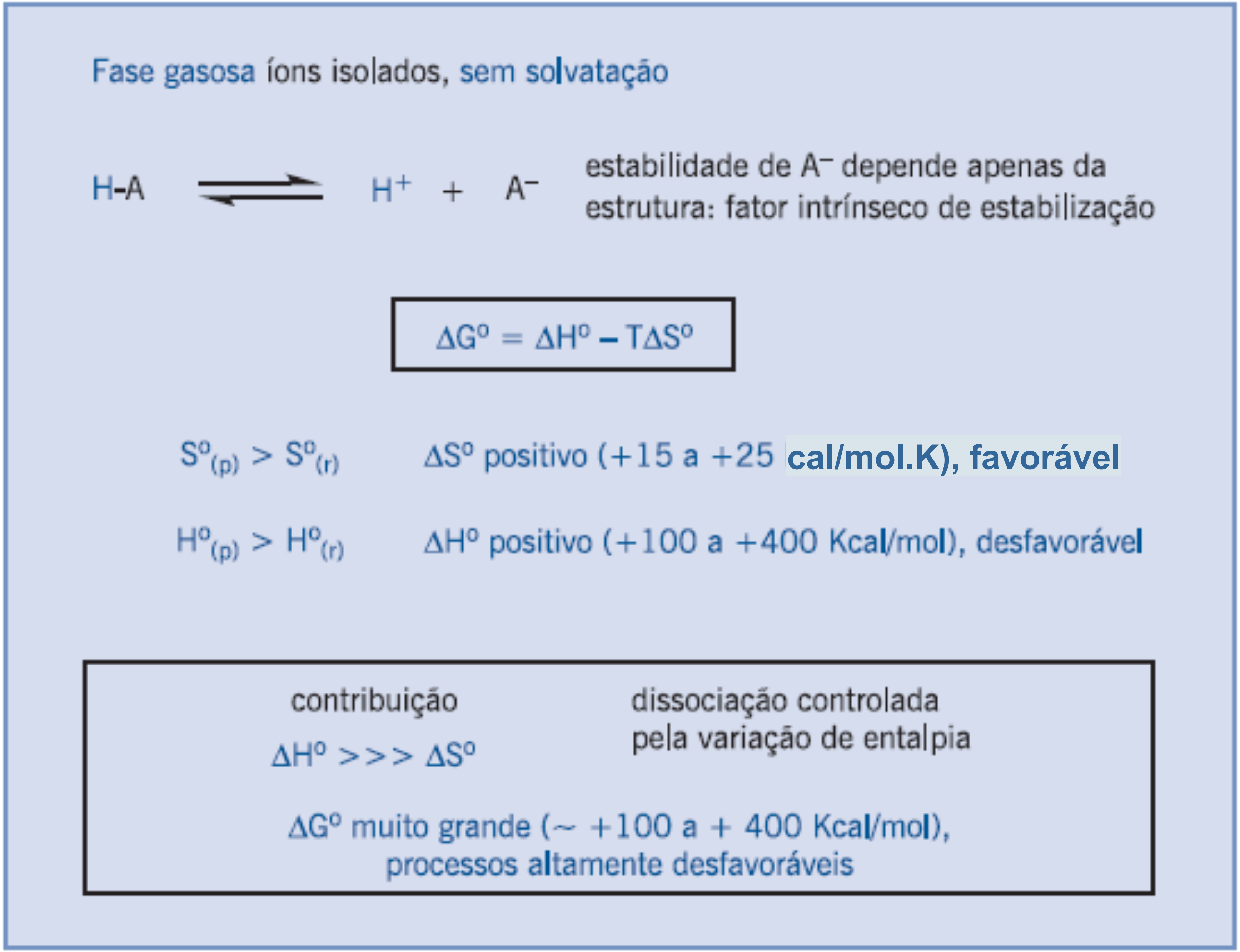
Alguns termos

Esquema 1.5 Exemplos de dissociações do ácido acético

ácido base ácido conjugado base conjugada

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

$$CH_3CO_2H + H_3N \longrightarrow H_4N^+ + CH_3CO_2^-$$



Fase gasosa íons isolados, sem solvatação

$H\text{-}A \rightleftharpoons H^+ + A^-$

estabilidade de A^- depende apenas da estrutura: fator intrínseco de estabilização

$$\boxed{\Delta G^o = \Delta H^o - T\Delta S^o}$$

$S^o_{(p)} > S^o_{(r)}$ ΔS^o positivo (+15 a +25 **cal/mol.K), favorável**

$H^o_{(p)} > H^o_{(r)}$ ΔH^o positivo (+100 a +400 Kcal/mol), desfavorável

contribuição

$\Delta H^o >>> \Delta S^o$

dissociação controlada pela variação de entalpia

ΔG^o muito grande (~ +100 a + 400 Kcal/mol), processos altamente desfavoráveis

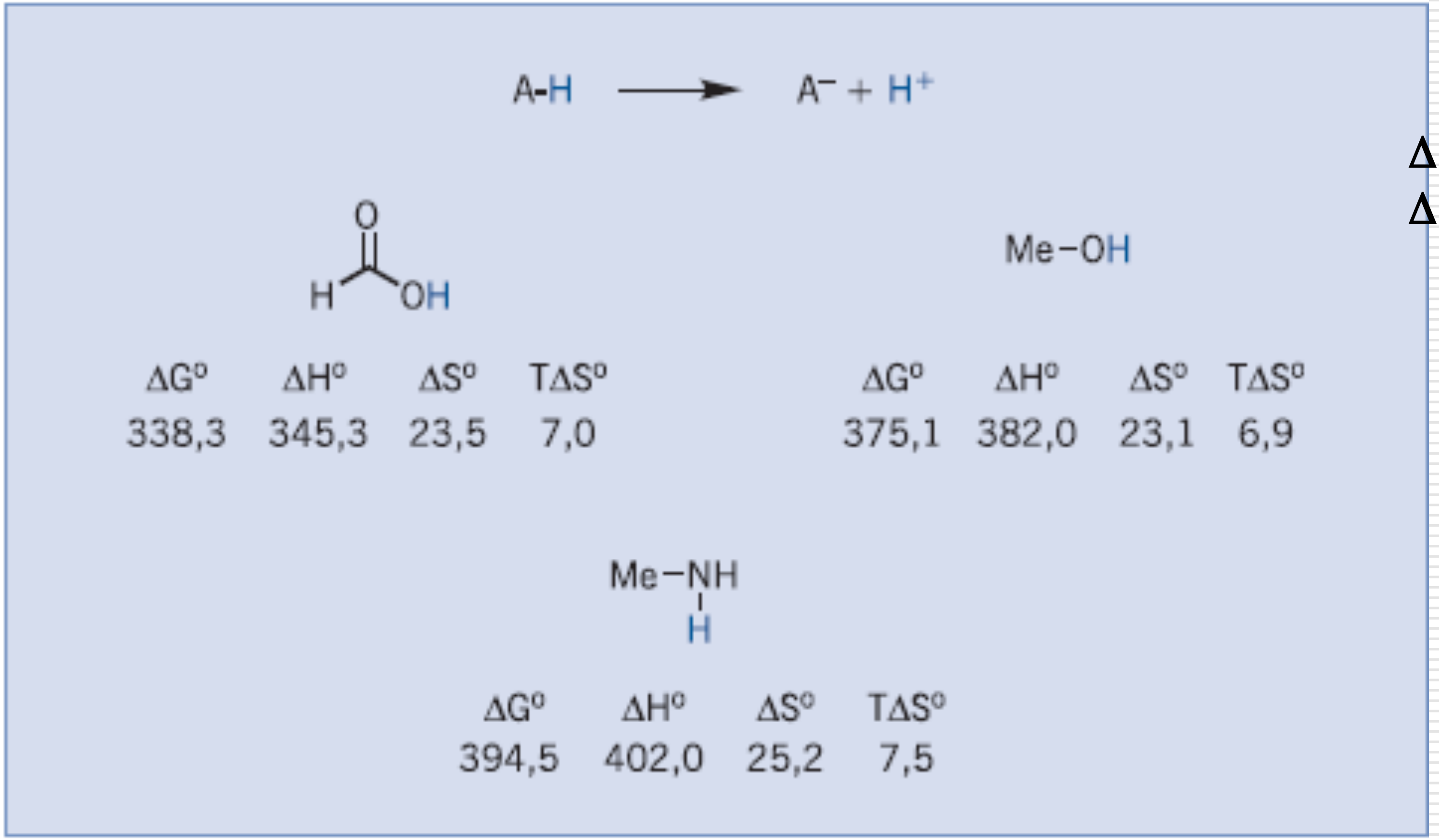
Fase gasosa

- Entalpia mais importante que entropia

↓

Dominado por fatores estruturais (estabilidade do de HA e de A^-)

Parâmetros Termodinâmicos para dissociação na fase gasosa



ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
338,3	345,3	23,5	7,0

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
375,1	382,0	23,1	6,9

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
394,5	402,0	25,2	7,5

ΔS^o varia pouco
ΔH^o domina

Efeitos Estruturais Intrísecos dominam

$[\Delta G^o]$= kcal/mol; $[\Delta H^o]$= kcal/mol; $[\Delta S^o]$= cal/mol.K; $[T\Delta S^o]$= kcal/mol

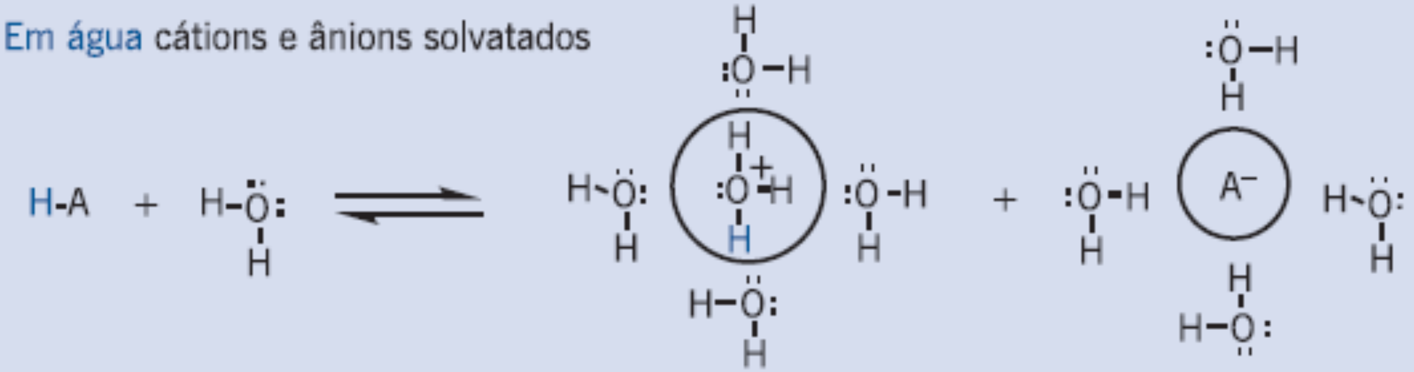
Em solução

- ΔH^o e $T\Delta S^o$ são comparáveis

↓

Acidez ($\Delta G^o = 1.4\ pK_a$, $T = 298K$) depende da **solvatação** e de fatores instrísecos (**estruturais**)

Em água cátions e ânions solvatados



solvatação nucleofílica

solvatação eletrofílica

ΔG^o, ΔH^o, $T\Delta S^o$
em Kcal/mol
ΔS^o em cal/mol·K

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$S^o_{(p)} < S^o_{(r)}$ $T\Delta S^o$ é negativo

$H^o_{(p)} < H^o_{(r)}$ ΔH^o positivo
ou
$H^o_{(p)} < H^o_{(r)}$ ΔH^o negativo

se a contribuição
$\Delta H^o > T\Delta S^o$ { dissociação controlada pela variação de entalpia

se a contribuição
$\Delta H^o < T\Delta S^o$ { dissociação controlada pela variação de entropia

ΔG^o pouco positivo ou negativo

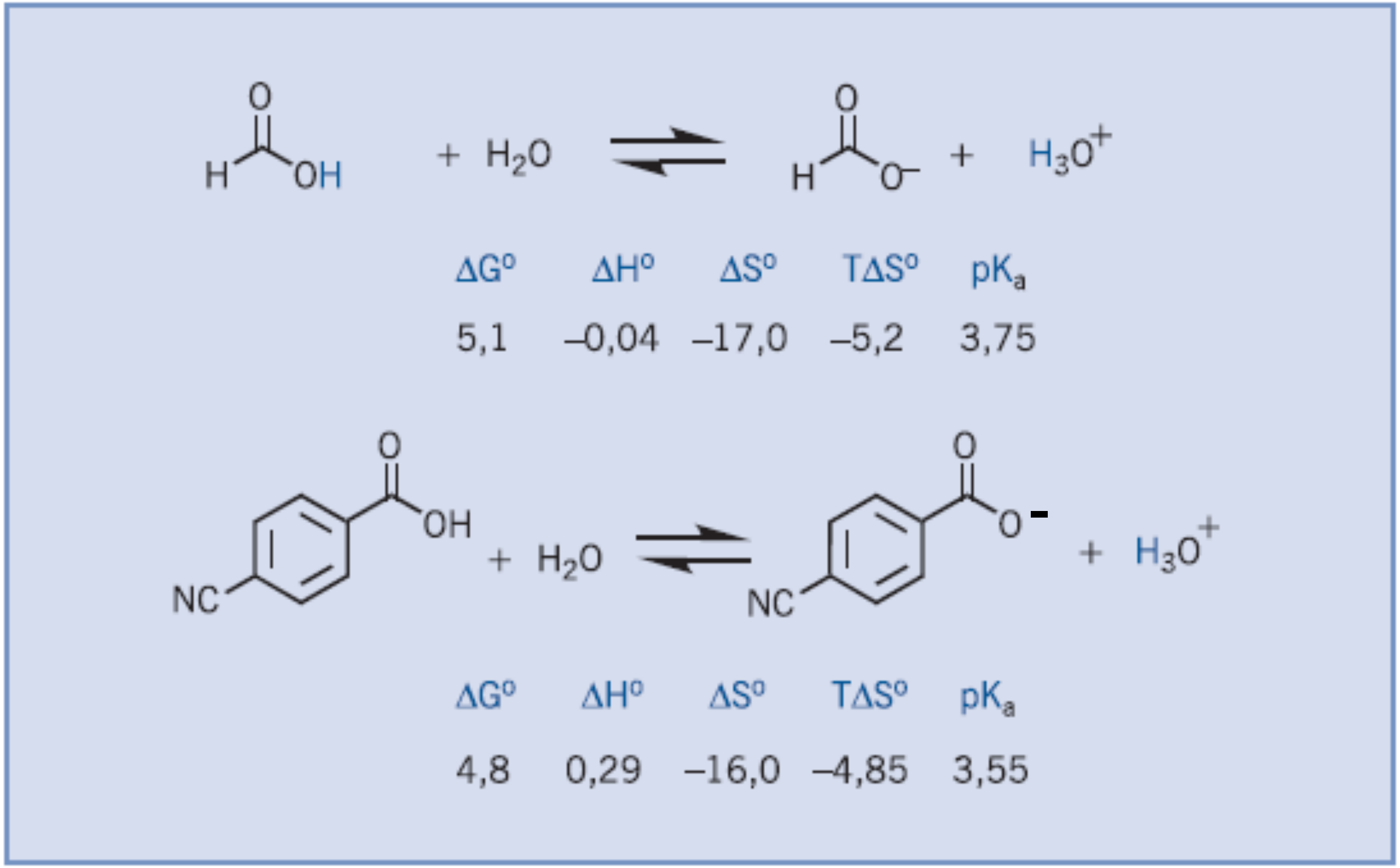
ΔG^o e posição do equilíbrio

- ***ΔG^o for menor -3.11 kcal/mol***

→ completamente deslocado no sentido dos produtos

- ***ΔG^o for maior +3.11 kcal/mol***

→ completamente deslocado no sentido dos reagentes



ESQUEMA 3.4 Parâmetros termodinâmicos para a dissociação do ácido fórmico e 4-cianobenzóico em água (ΔG°, ΔH°, TΔS° em Kcal/mol, ΔS° em cal/mol·K).

ΔG°	ΔH°	ΔS°	TΔS°	pK_a
5,1	–0,04	–17,0	–5,2	3,75

ΔG°	ΔH°	ΔS°	TΔS°	pK_a
4,8	0,29	–16,0	–4,85	3,55

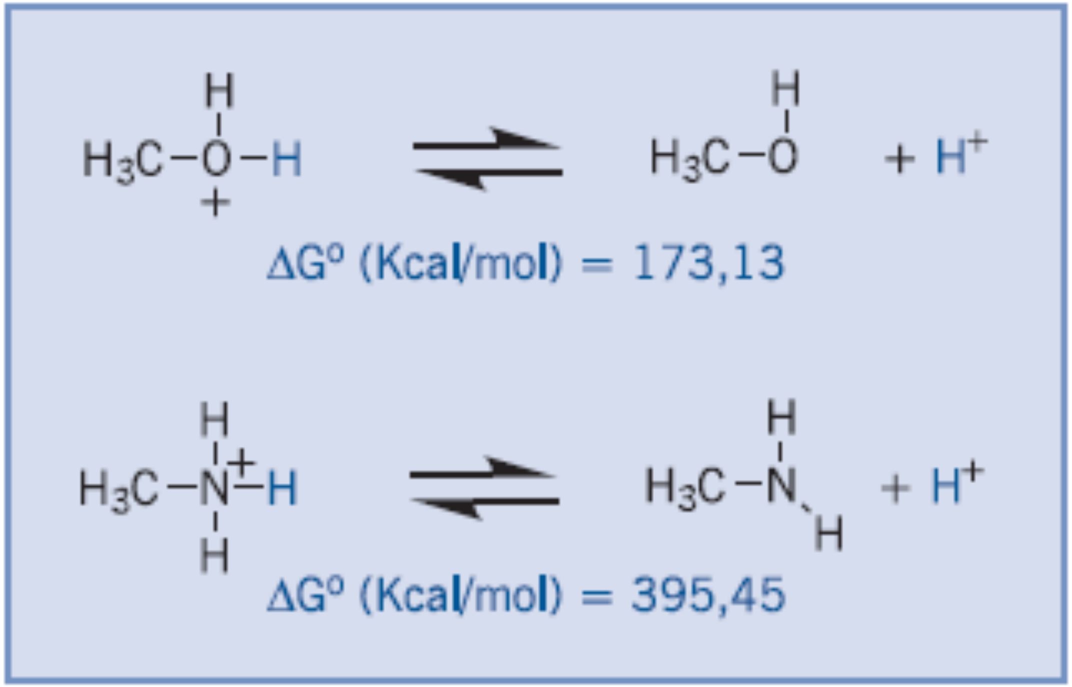
Controlado pelo fator entrópico (TΔSº)

[ΔGº]= kcal/mol; [ΔHº]= kcal/mol; [ΔSº]= cal/mol.K; [TΔSº]= kcal/mol

Organização do solvente em torno dos íons faz o termo entrópico desfavorável

Se os reagentes forem iônicos

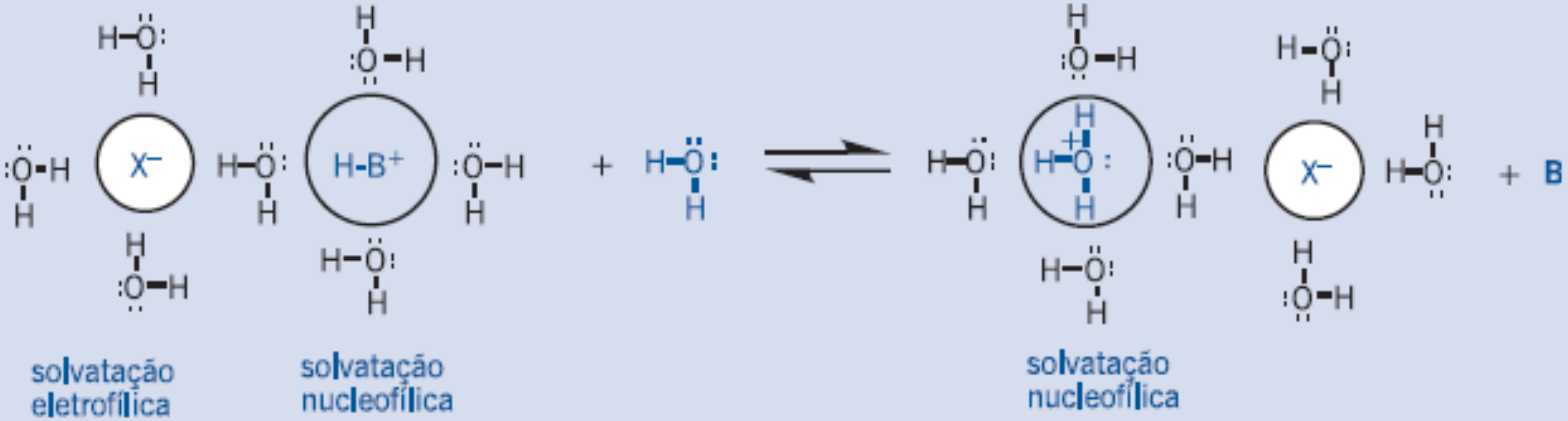
- Na fase gasosa entropia parecida (um corpo (BH^+) gerando dois corpos ($B + H^+$)
- Entalpia governa processo



ESQUEMA 3.6 Parâmetros termodinâmicos para a dissociação do metanol e da metilamina protonados em fase gasosa.

$$HB^{+}\ X^{-} + H_2O \xrightleftharpoons{H_2O} B + H_3O^{+}\ X^{-}$$

Em água cátions e ânions solvatados



$$\boxed{\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}}$$

$S^{o}_{(p)} > S^{o}_{(r)} \longrightarrow T\Delta S^{o}$ positivo

$S^{o}_{(p)} < S^{o}_{(r)} \longrightarrow T\Delta S^{o}$ negativo

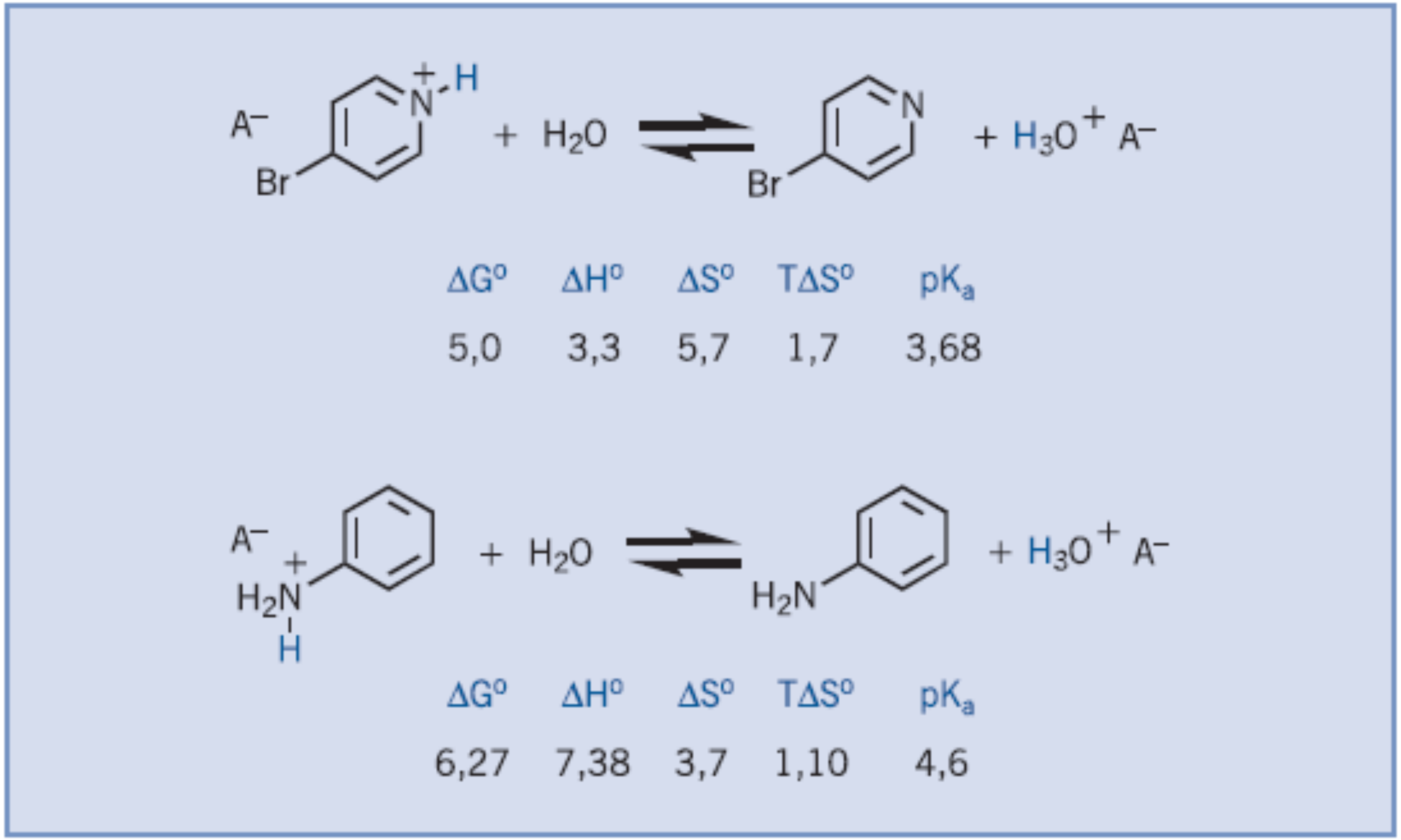
$H^{o}_{(p)} > H^{o}_{(r)}$

$\Delta H^{o} \longrightarrow$ positivo

ΔG° controlado entalpicamente ou
entropicamente, dependendo da
contribuição de cada termo

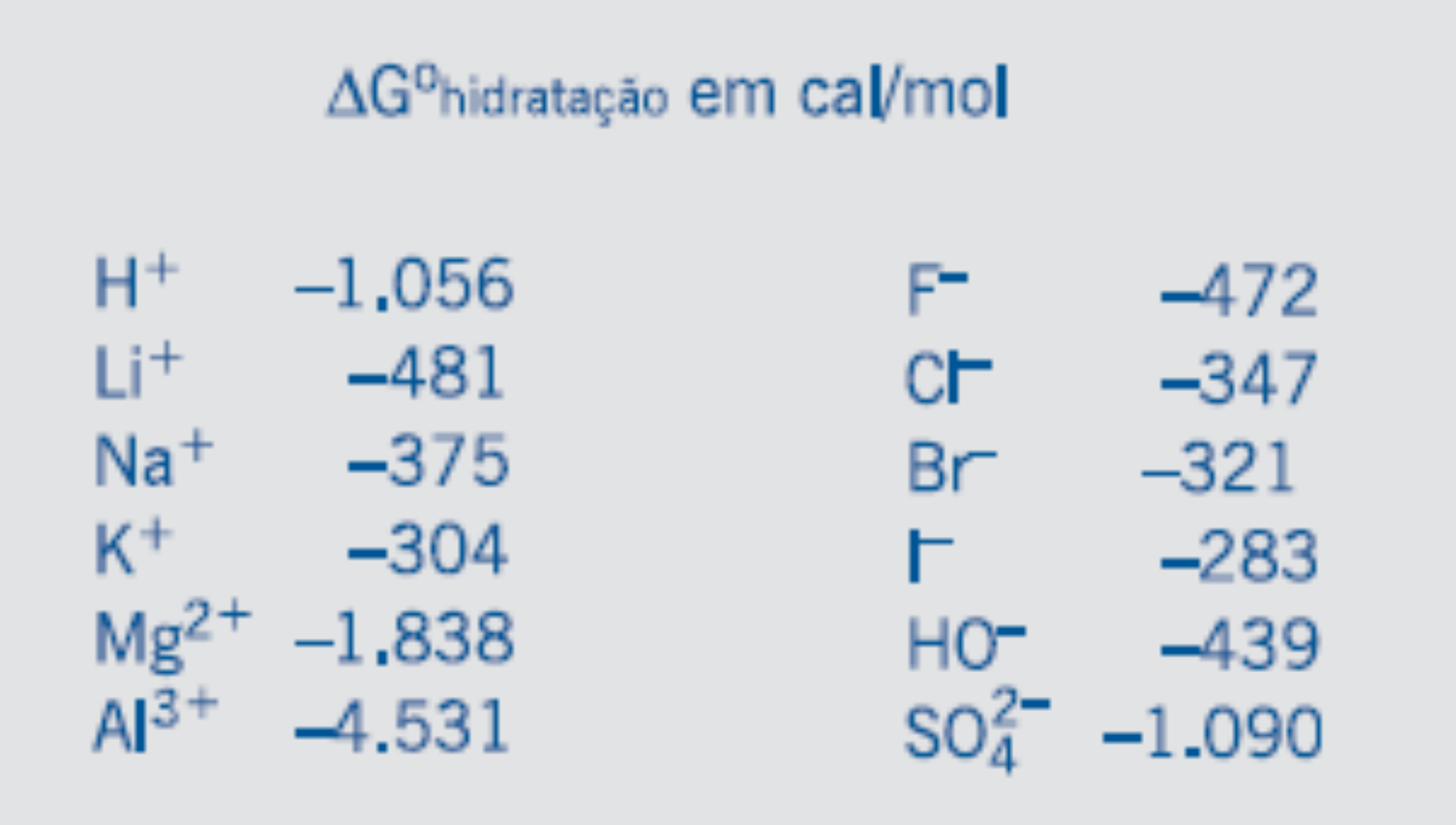
Em água

- Termo entrópico vai depender da solvatação diferencial entre reagentes (BH^+ e H_2O) e dos produtos (B e H_3O^+)



ESQUEMA 3.8 Parâmetros termodinâmicos para a dissociação do 4-bromopiridínio e do anilínio em água (ΔG°, ΔH° e TΔS° em Kcal/mol e ΔS° em cal/mol·K).

Energias de solvatação de alguns íons

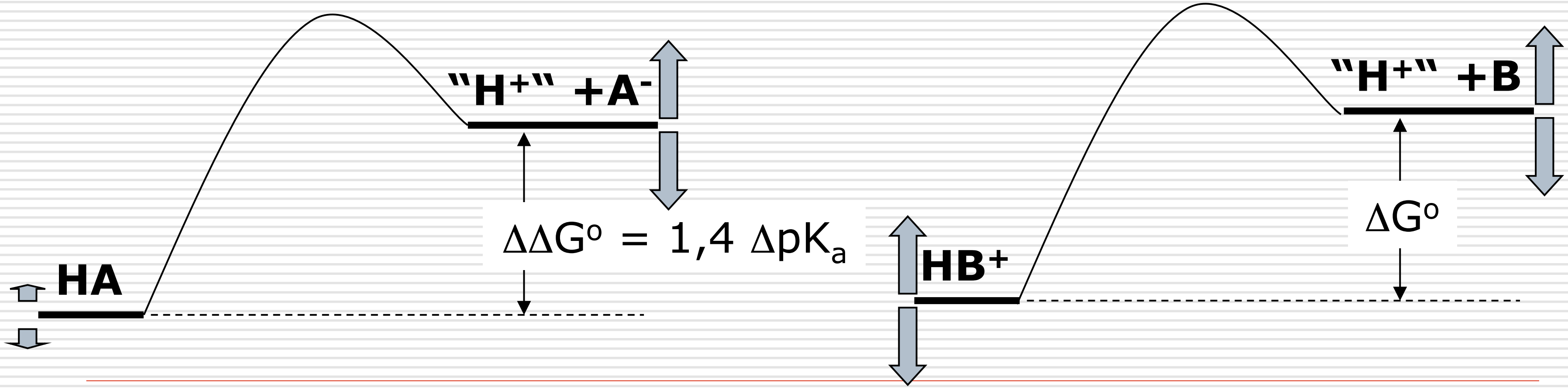


$\Delta G^{o}_{\text{hidratação}}$ em cal/mol

H^+	–1.056	F^-	–472
Li^+	–481	Cl^-	–347
Na^+	–375	Br^-	–321
K^+	–304	I^-	–283
Mg^{2+}	–1.838	HO^-	–439
Al^{3+}	–4.531	SO_4^{2-}	–1.090

Efeitos de solvente

- Solvatação é muito mais importante para espécies carregadas (íons)
- Moléculas neutras são menos suceptíveis à efeitos de solvatação



HA

"H^+" +A^-

$\Delta\Delta G^o = 1{,}4\ \Delta pK_a$

HB^+

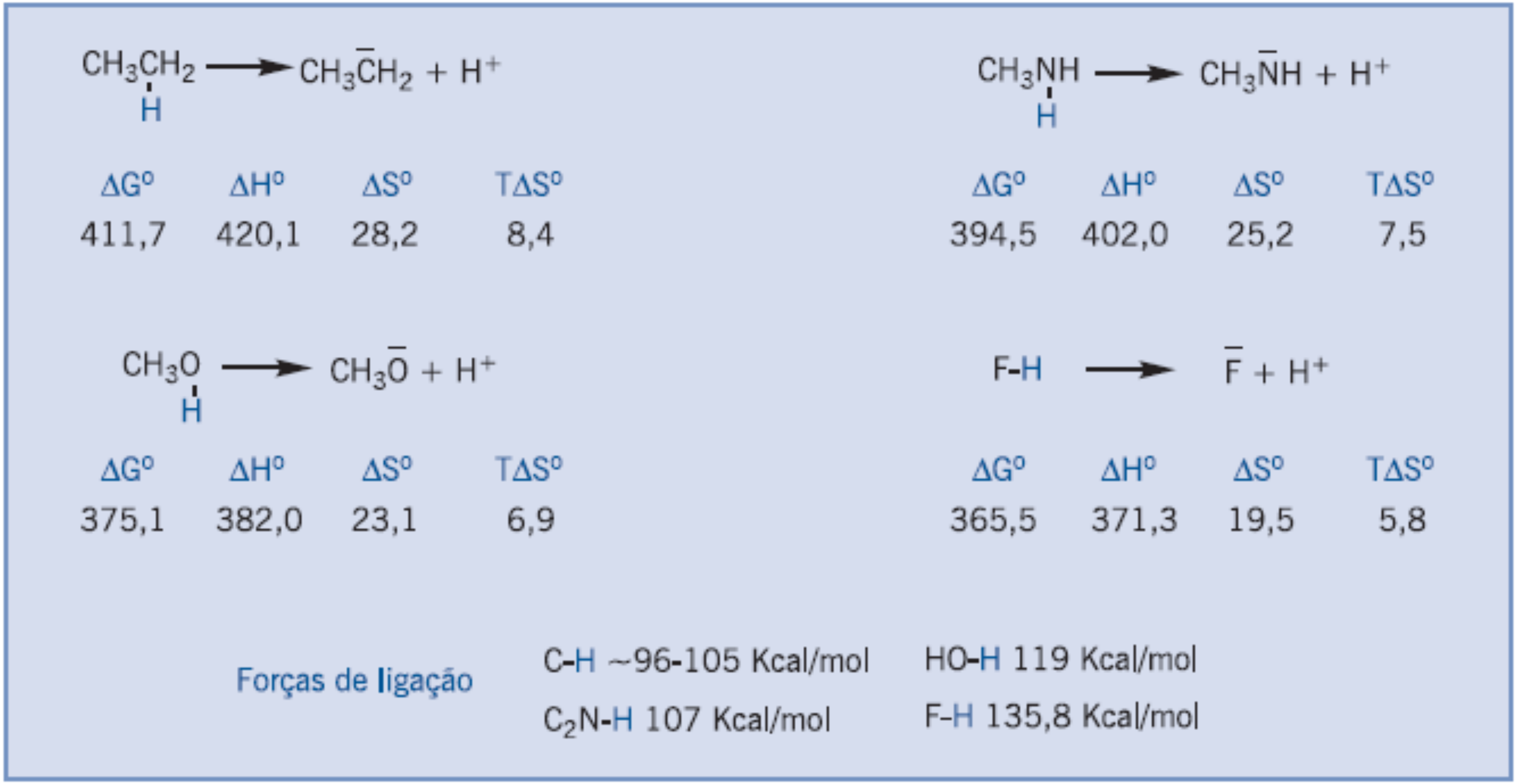
"H^+" +B

ΔG^o

Fatores Instrísecos que afetam a basicidade

- Eletronegatividade
- Volume do átomo ligado ao hidrogênio
- Hibridação
- Efeito Polar
- Efeito Ressonância

Eletronegatividade



$CH_3\underset{H}{C}H_2 \longrightarrow CH_3\bar{C}H_2 + H^+$

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
411,7	420,1	28,2	8,4

$CH_3\underset{H}{N}H \longrightarrow CH_3\bar{N}H + H^+$

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
394,5	402,0	25,2	7,5

$CH_3\underset{H}{O} \longrightarrow CH_3\bar{O} + H^+$

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
375,1	382,0	23,1	6,9

$F\text{-}H \longrightarrow \bar{F} + H^+$

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
365,5	371,3	19,5	5,8

Forças de ligação

C-H ~96-105 Kcal/mol

C_2N-H 107 Kcal/mol

HO-H 119 Kcal/mol

F-H 135,8 Kcal/mol

ESQUEMA 3.9 Dissociação em fase gasosa (Kcal/mol) para ligações C-H, O-H, N-H e F-H (ΔG^o, ΔH^o e $T\Delta S^o$ em Kcal/mol e ΔS^o em cal/mol·K).

pK_a

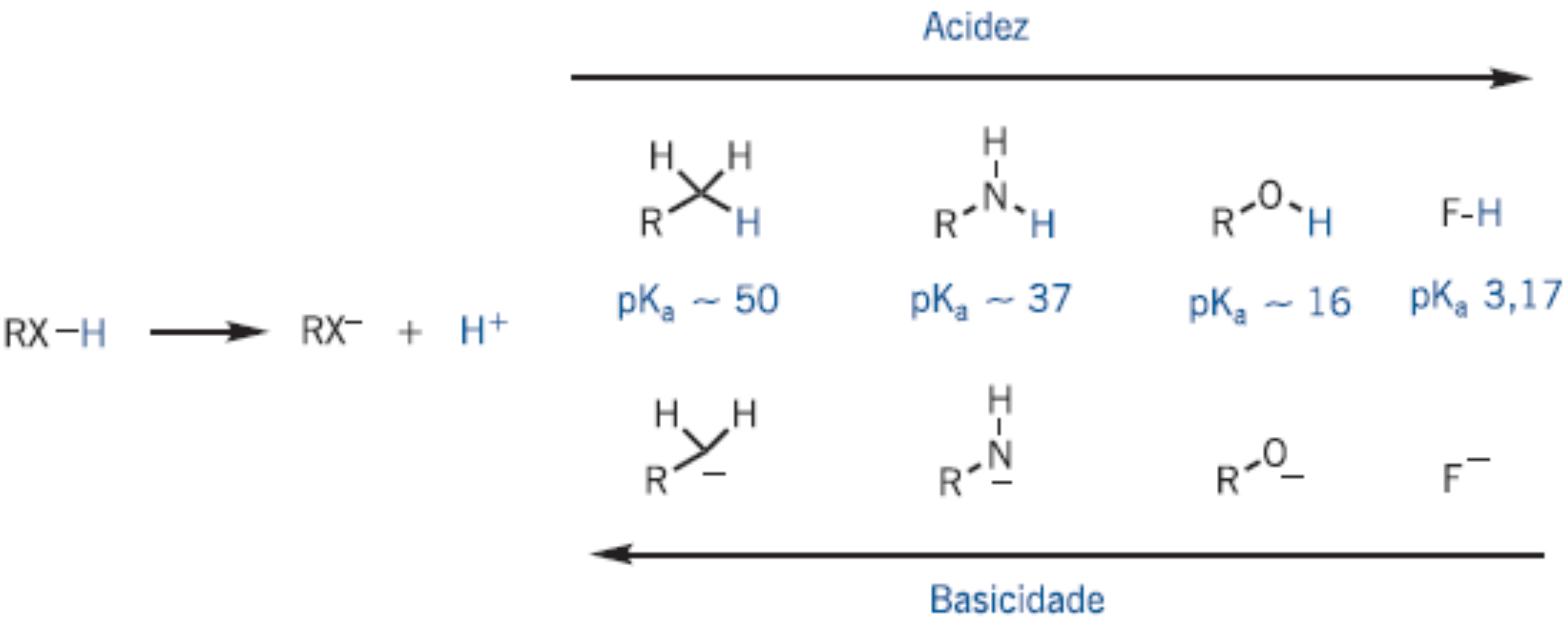
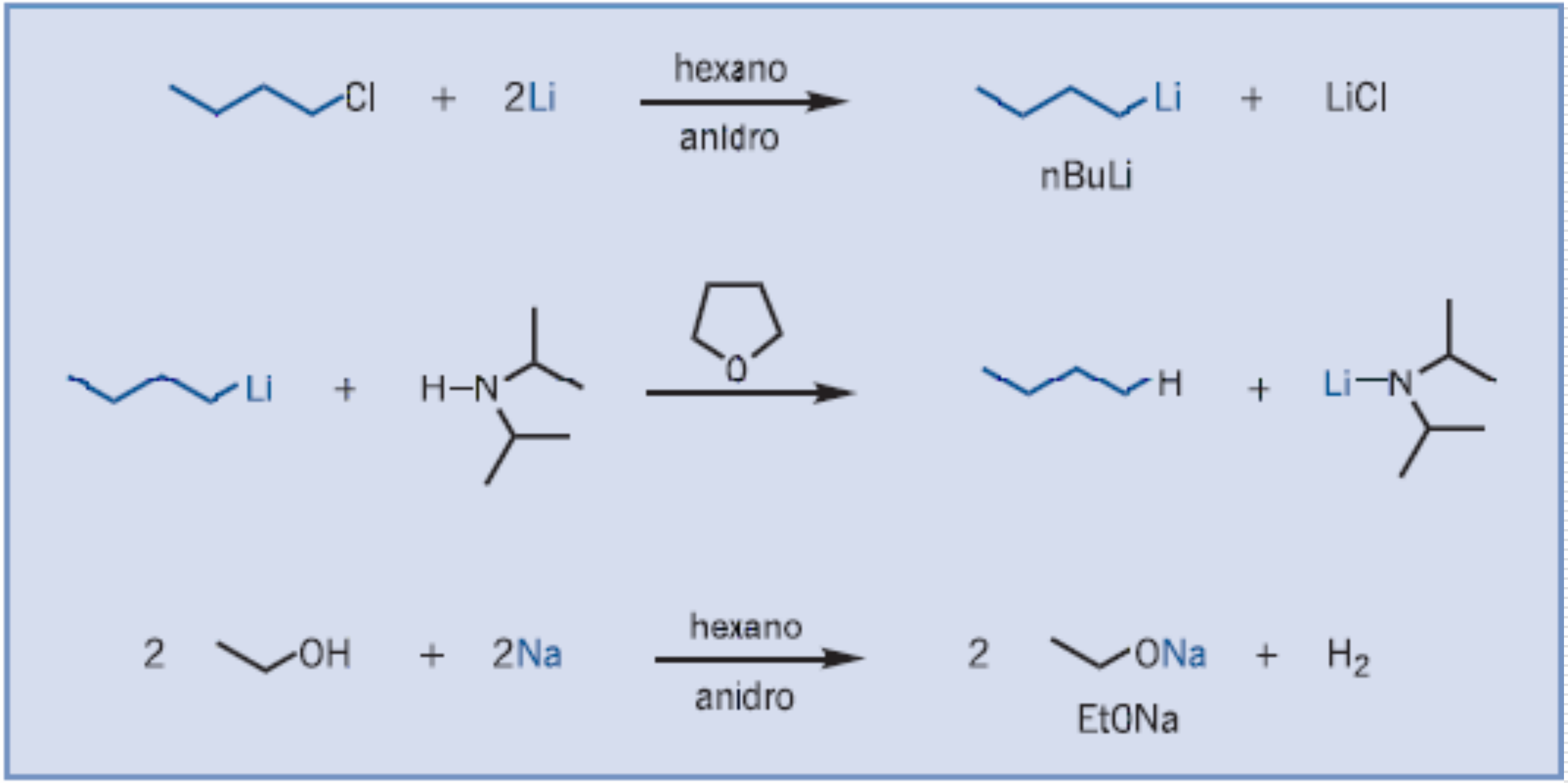


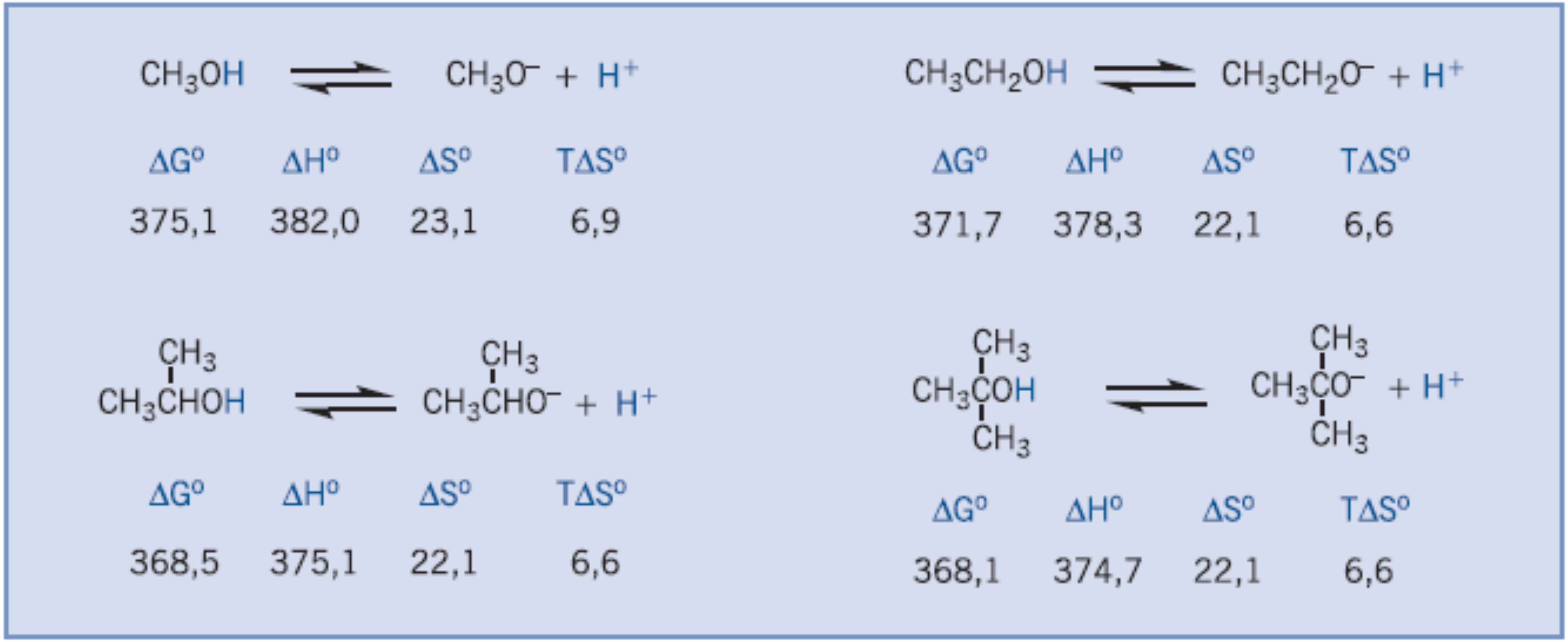
FIGURA 3.1 Comparação dos valores de pK_a para alcanos, aminas, alcoóis e HF.

Formação de Amidetos e Alcóxidos



Volume molecular: Ordem fase gasosa t-BuOH > i-PrOH > EtOH > MeOH

Mais ácido ← **Menos ácido**



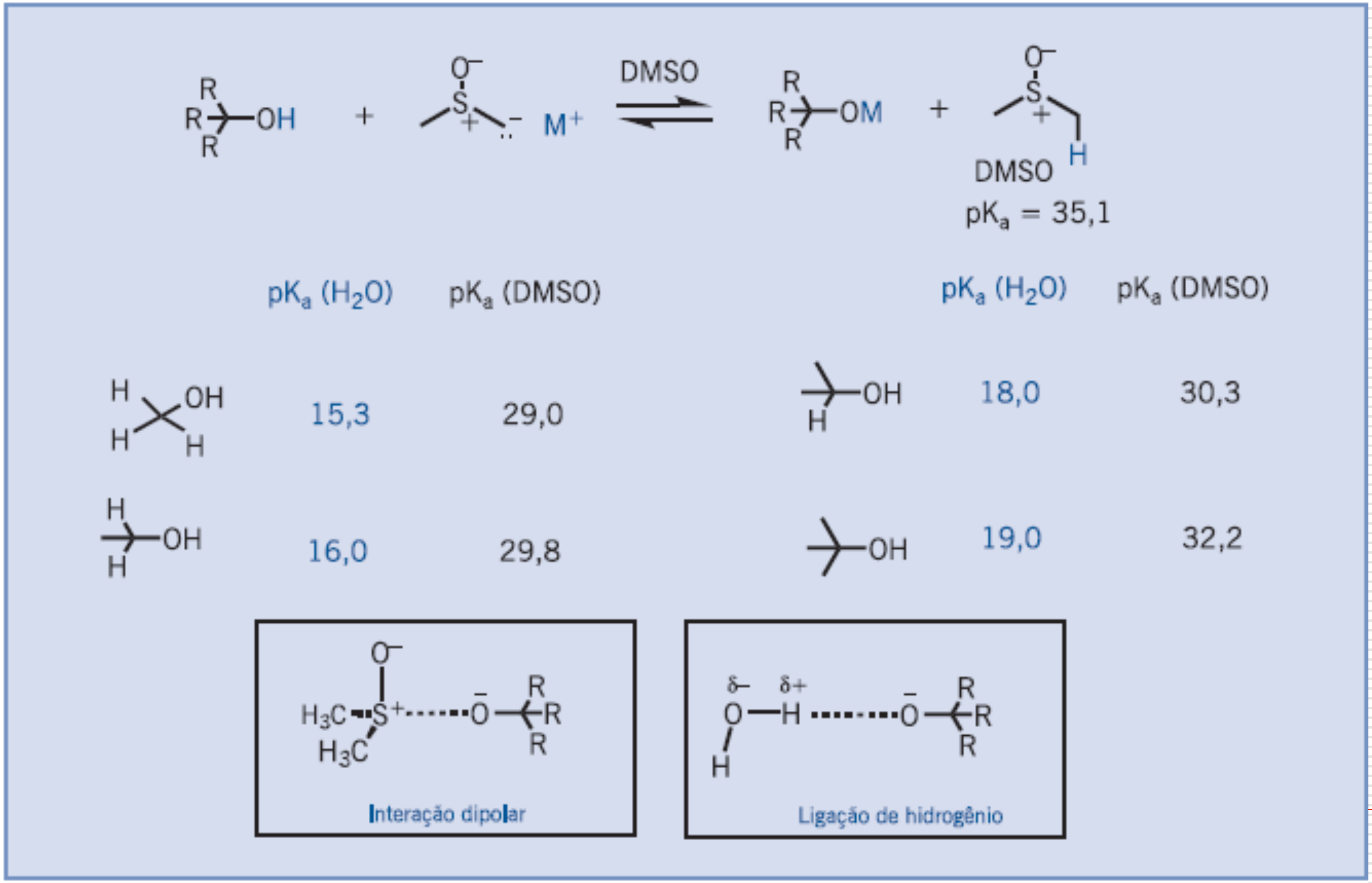
ESQUEMA 3.11 Dissociação de alcoóis em fase gasosa (ΔG°, ΔH° e TΔS° em Kcal/mol e ΔS° em cal/mol·K).

- Ânions volumosos são mais estáveis
- Maior superfície molecular aumenta distância média entre elétrons levando a uma diminuição da repulsão carga-carga

↓

Abaixamento da energia potencial (ΔH°)

Volume molecular: Ordem em DMSO MeOH > EtOH > i-PrOH > t-BuOH



ESQUEMA 3.12 Dissociação de alcoóis em DMSO-Dimsil M.

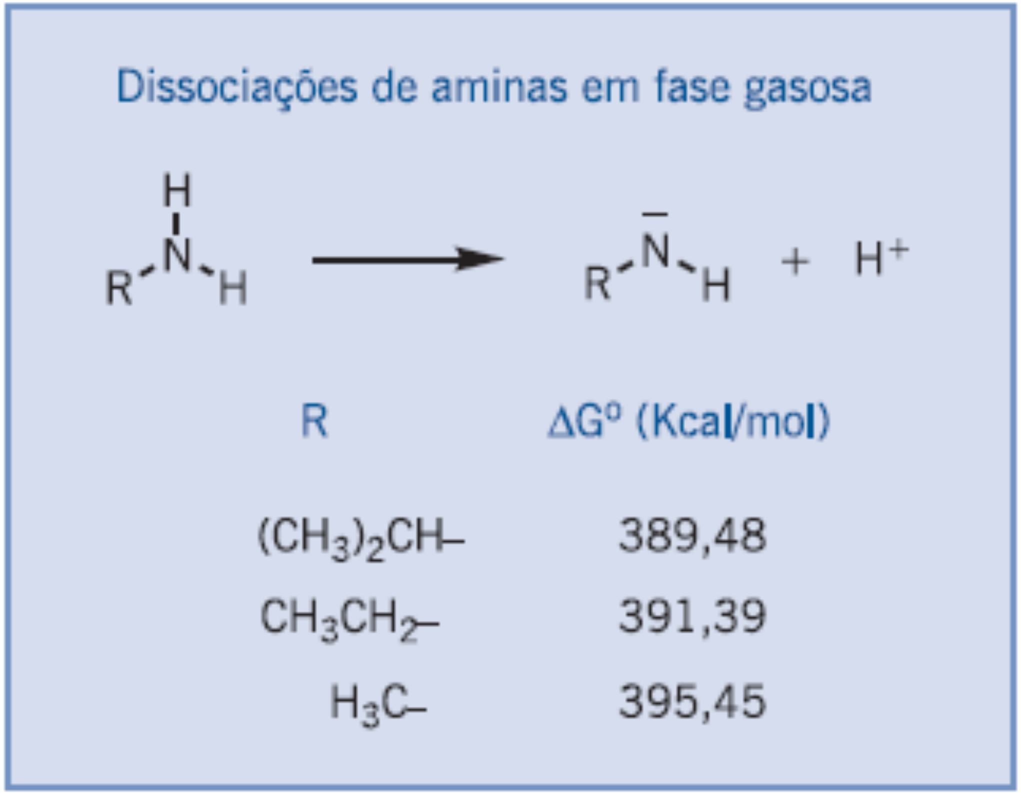
Porquê ordem de acidez inverte?

- Efeitos de solvente

- Interpretação que t-BuOH é menos ácido que MeOH devido ao efeito indutivo doador de elétrons do grupo metila, desestabilizando o alcóxido, está **errada**!!!

Aminas

- Aumento da superfície molecular do ânion o estabiliza

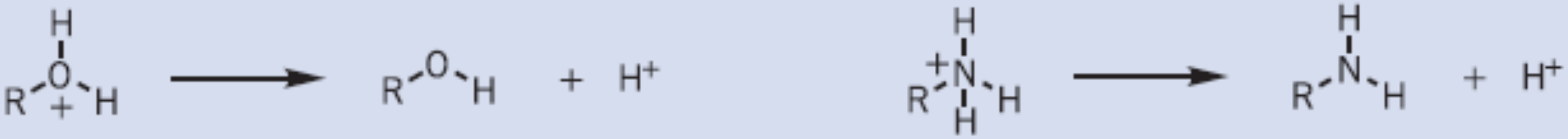


Dissociações de aminas em fase gasosa

R	ΔG° (Kcal/mol)
$(CH_3)_2CH-$	389,48
CH_3CH_2-	391,39
H_3C-	395,45

ESQUEMA 3.13 Dissociação de aminas em fase gasosa.

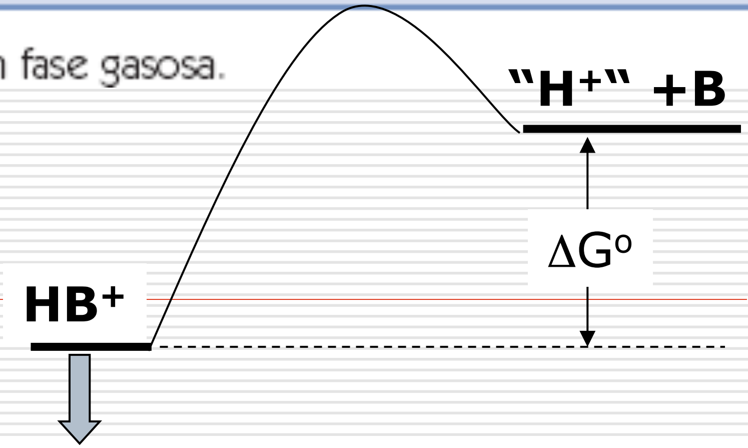
Oxônios x Alquilamônios



R	ΔG^o (Kcal/mol)	R	ΔG^o (Kcal/mol)
$(CH_3)_3C-$	184,35	$(CH_3)_3C-$	214,92
$(CH_3)_2CH-$	182,20	$(CH_3)_2CH-$	212,29
CH_3CH_2-	178,14	CH_3CH_2-	209,67
H_3C-	157,61	H_3C-	206,56

ESQUEMA 3.14 Dissociações de hidrônios e amônios em fase gasosa.

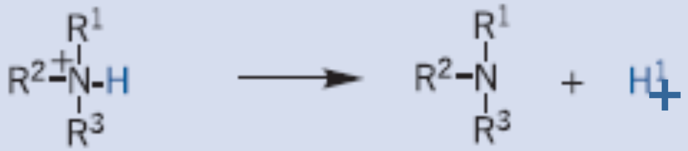
$\Delta G^o = 1,4\ pK_a$



Aumento superfície Oxônio/alquilamônio

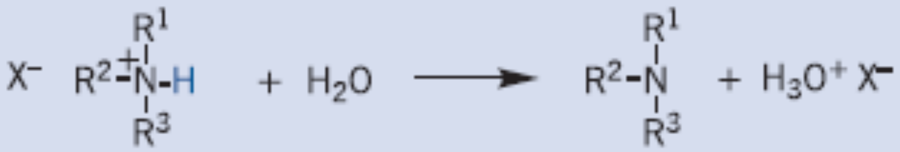
Outros alquilamônios

fase gasosa



$$R^1R^2R^3NH^+ \longrightarrow R^1R^2R^3N + H^+$$

água



$$X^- \; R^1R^2R^3NH^+ + H_2O \longrightarrow R^1R^2R^3N + H_3O^+ X^-$$

	fase gasosa				água				
	ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$	ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$	
$R^1=R^2=R^3=H$	195,7	204,0	27,8	8,3	12,6	12,4	0,7	+0,2	pK_a = 9,24
R^1=Me, $R^2=R^3=H$	206,6	214,9	27,8	8,3	14,4	13,0	–5,0	–1,4	pK_a = 10,62
$R^1=R^2$=Me, $R^3=H$	214,3	222,2	26,5	7,9	14,7	11,8	–9,5	–2,84	pK_a = 10,77
$R^1=R^2=R^3$=Me	219,4	226,8	24,8	7,4	13,3	8,8	–15,0	–4,47	pK_a = 9,80

ESQUEMA 3.15 Dissociação de íons amônio e alquilamônio em fase gasosa e em água (ΔG°, ΔH° e TΔS° em Kcal/mol e ΔS° em cal/mol·K).

Solvatação dos cátions R_3NH^+ (R=H,alquila)

- Entalpia e entropia disputam controle do equilíbrio
- NH_4^+ e H_3O^+ são semelhantes
  - $T\Delta S^o$ = +0,2 kcal/mol (pequeno)
  - $NH_4^+ \rightarrow$ 4 ligações de hidrogênio
  - $H_3O^+ \rightarrow$ 3 ligações de hidrogênio
- Quanto menos solvatado o R_3NH^+, no estado inicial (menor nº de lig. hidrogênio), maior a organização que o solvente sofre quando passa a solvatar o H_3O^+

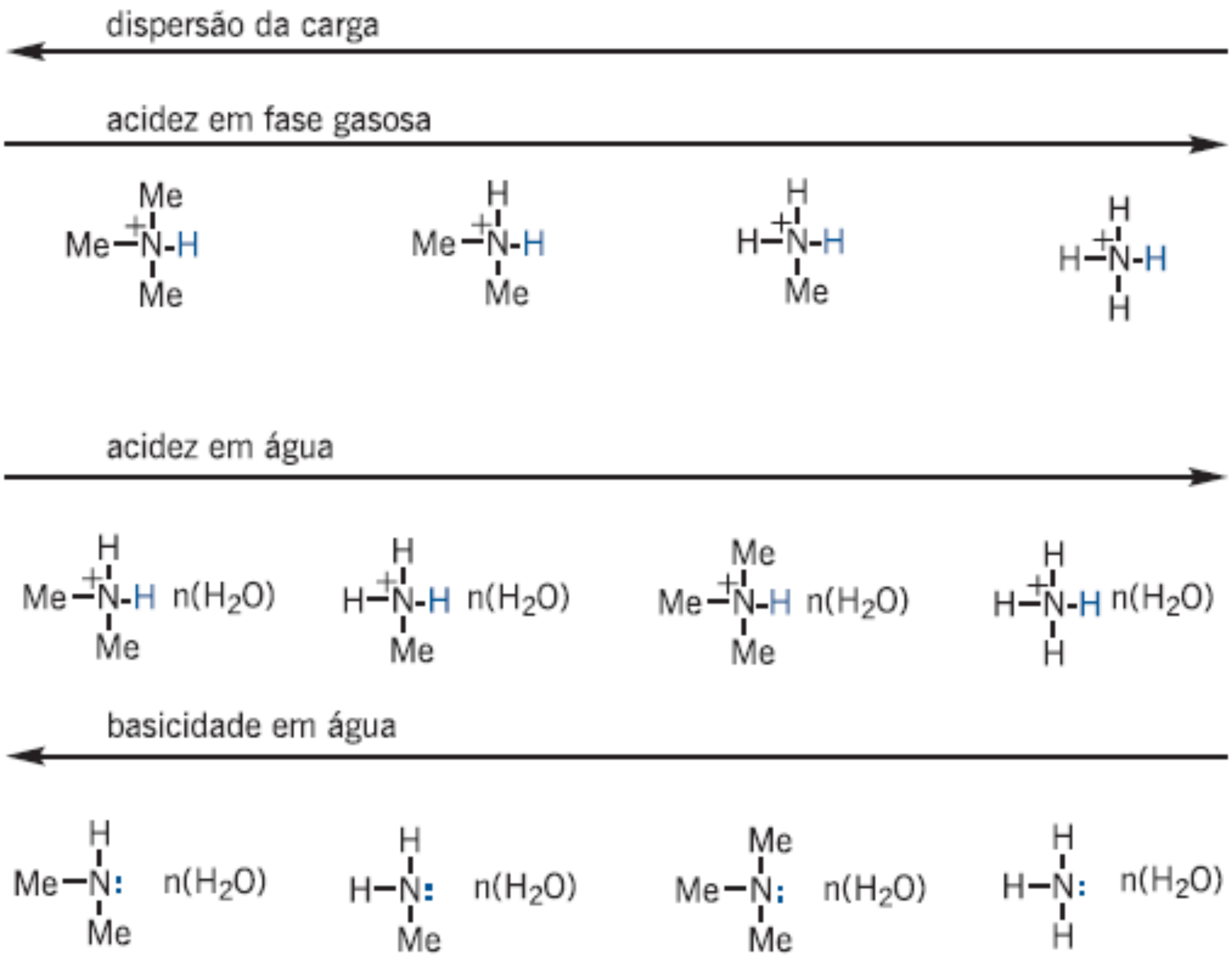
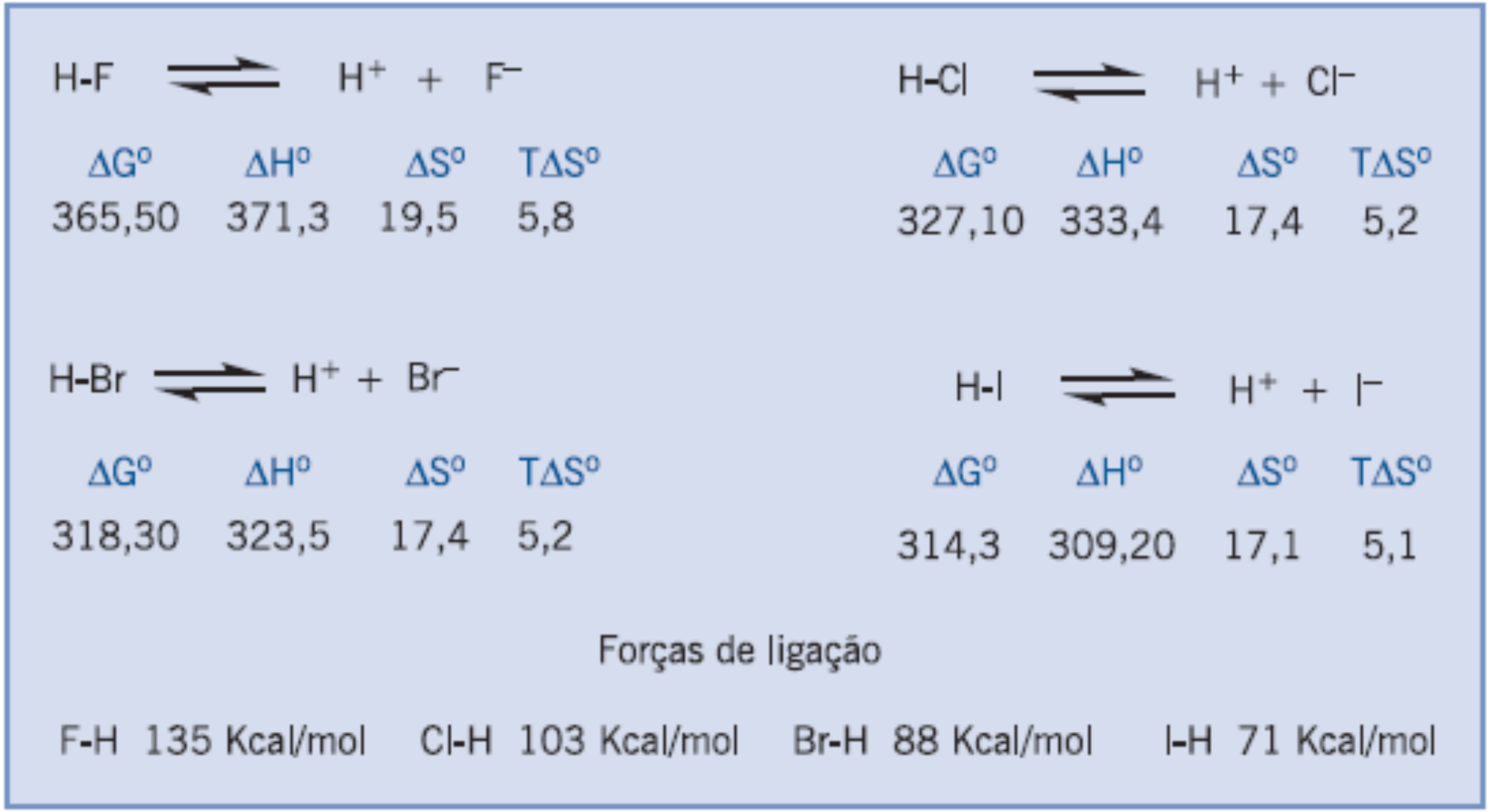


FIGURA 3.2 Basicidade de aminas em fase gasosa e em água.

Volume do átomo ligado ao hidrogênio



$\text{H-F} \rightleftharpoons \text{H}^+ + \text{F}^-$

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
365,50	371,3	19,5	5,8

$\text{H-Cl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
327,10	333,4	17,4	5,2

$\text{H-Br} \rightleftharpoons \text{H}^+ + \text{Br}^-$

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
318,30	323,5	17,4	5,2

$\text{H-I} \rightleftharpoons \text{H}^+ + \text{I}^-$

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
314,3	309,20	17,1	5,1

Forças de ligação

F-H 135 Kcal/mol   Cl-H 103 Kcal/mol   Br-H 88 Kcal/mol   I-H 71 Kcal/mol

ESQUEMA 3.16 Dissociação de ácidos halogenídricos em fase gasosa (ΔG^o, ΔH^o e $T\Delta S^o$ em Kcal/mol e ΔS^o em cal/mol·K).

- Maior área superficial no haleto estabiliza produto

Ácidos halogenídricos

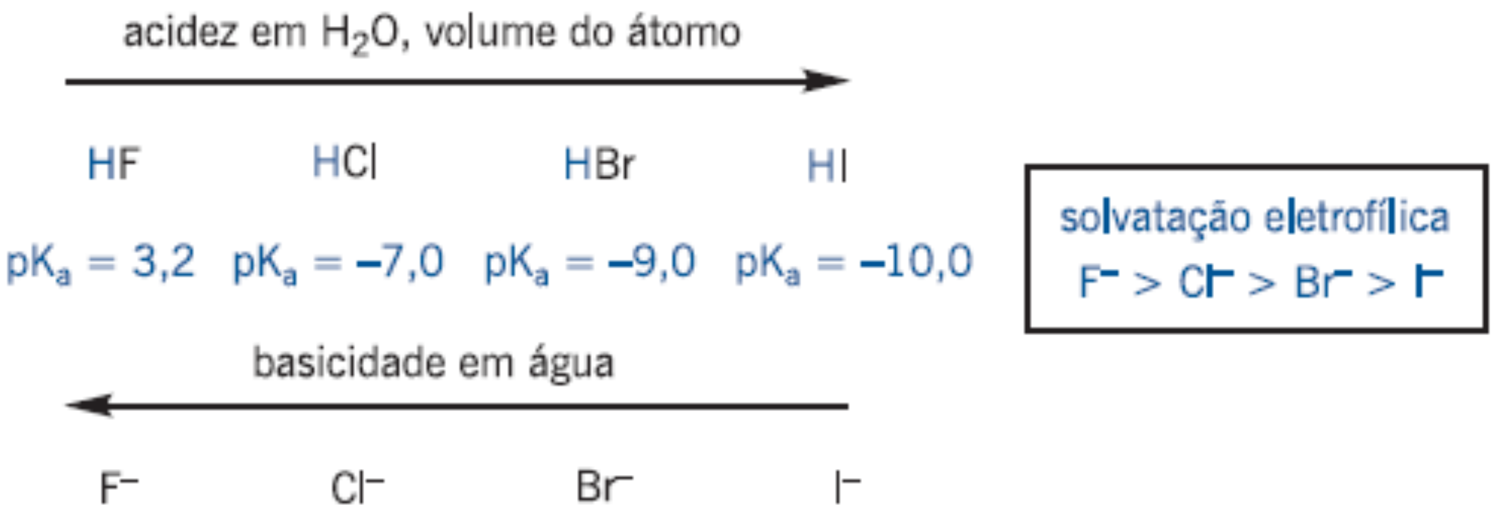


FIGURA 3.3 Dissociação de ácidos halogenídricos em água.

- Maior solvatação do F^- levaria a uma maior estabilização deste (ΔH^o).
- Entretanto organiza mais o solvente quando dissociado, desfavorecendo a dissociação pelo fator entrópico ($T\Delta S^o$).

S x O

$MeSH \rightleftharpoons H^+ + MeS^-$

ΔG°	ΔH°	ΔS°	TΔS°
350,6	357,6	23,5	7,0

$EtSH \rightleftharpoons H^+ + MeS^-$

ΔG°	ΔH°	ΔS°	TΔS°
348,9	355,7	22,8	6,8

$MeOH \rightleftharpoons H^+ + MeO^-$

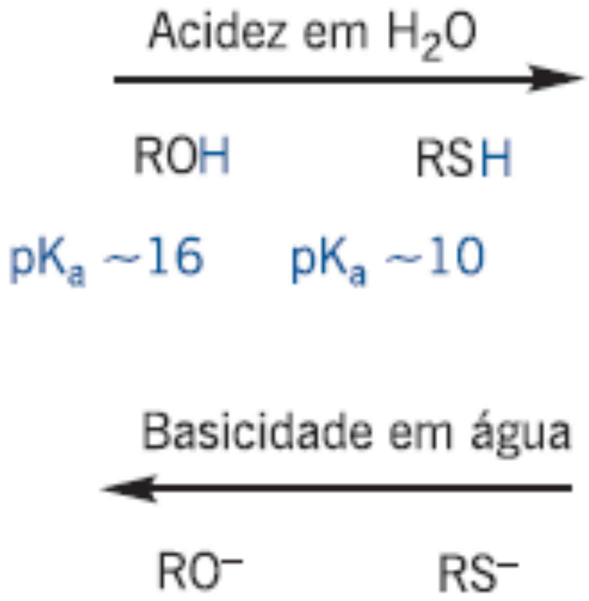
ΔG°	ΔH°	ΔS°	TΔS°
375,1	382,0	23,1	6,9

$EtOH \rightleftharpoons H^+ + MeO^-$

ΔG°	ΔH°	ΔS°	TΔS°
371,7	378,3	22,1	6,6

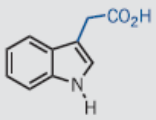
ESQUEMA 3.17 Dissociação de alcoóis e tióis em fase gasosa (ΔG°, ΔH° e TΔS° em Kcal/mol e ΔS° em cal/mol·K).

- ☐ Maior área superficial do S em relação ao O faz os tióis mais ácidos



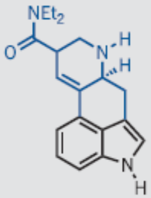
Solvatação eletrofílica
$RO^- > RS^-$

FIGURA 3.4 Dissociação de alcoóis e tióis em água.



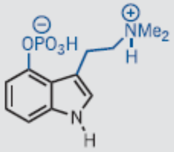
ácido indolacético

Hormônio do crescimento de plantas



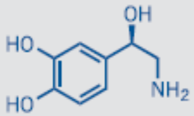
LSD

Derivado do ácido lisérgico isolado do fungo *Claviceps purpurea*, um contaminante comum do centeio e outros cereais

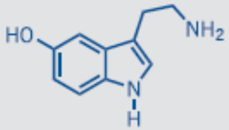


psilocibina

Isolada de *Psylocibe mexicana*, *Psilocybe muscorumi* e *Stropharia cubensis* (alucinógeno, cogumelos mágicos)

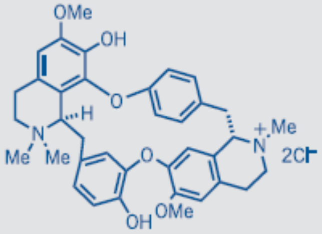


nor-adrenalina
neurotransmissor
periférico e central

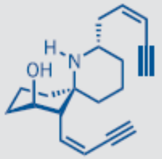


serotonina
neurotransmissor
central

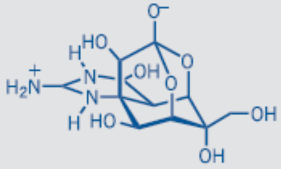
acetilcolina
neurotransmissor
periférico e central



Hidrocloreto de Tubocuranina (curare)

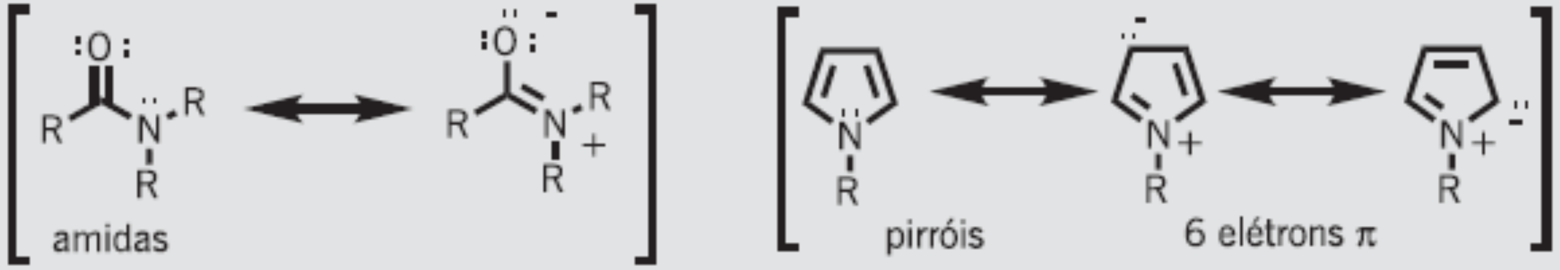


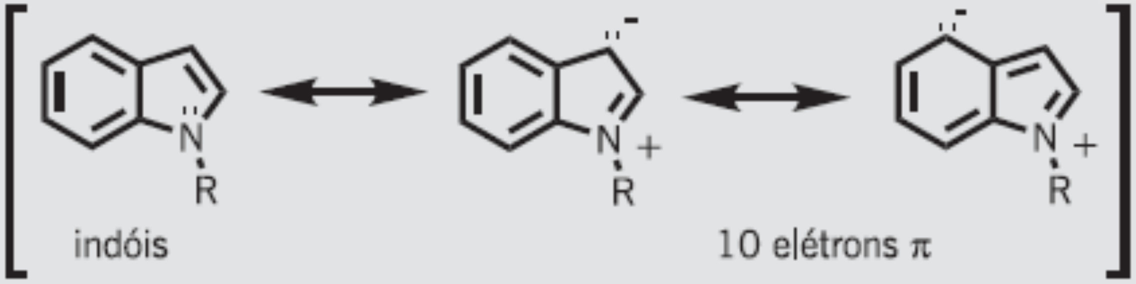
Histrionicotoxina



Tetrodotoxina (TTX)

Basicidade de amidas, pirróis e indóis

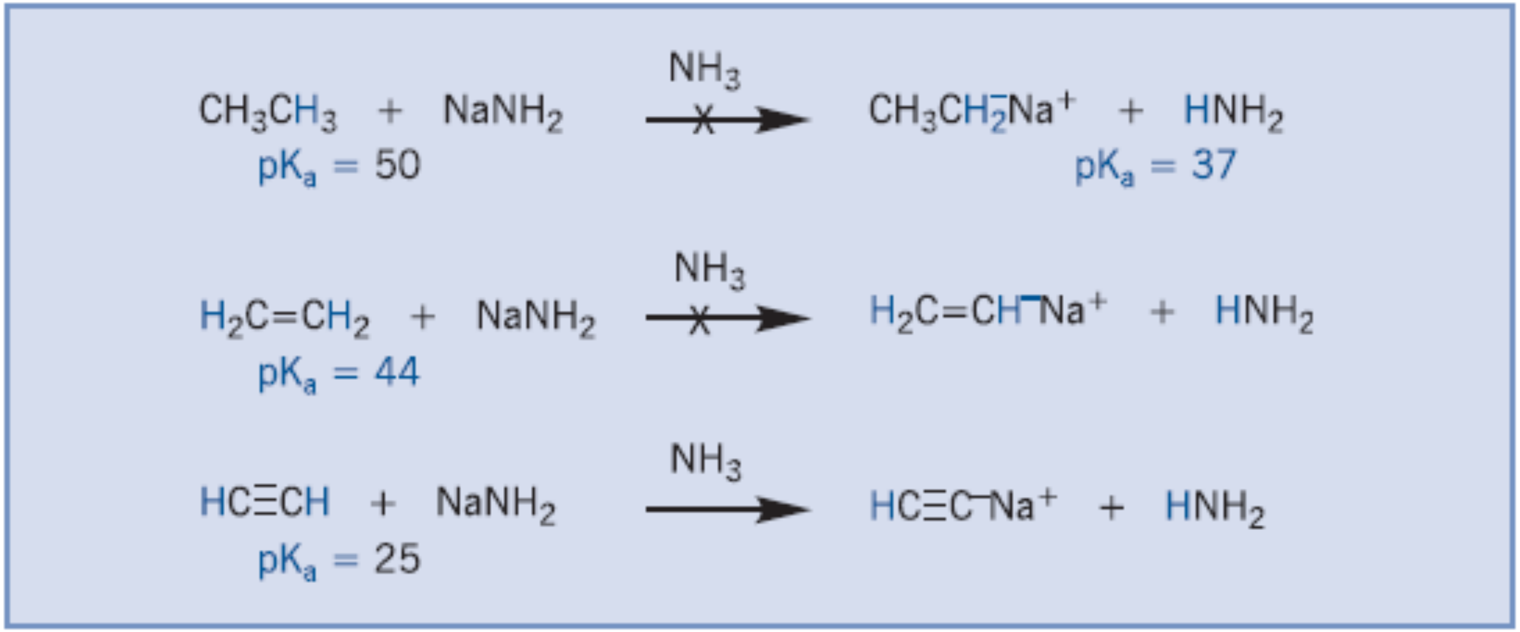




regra de Huckel

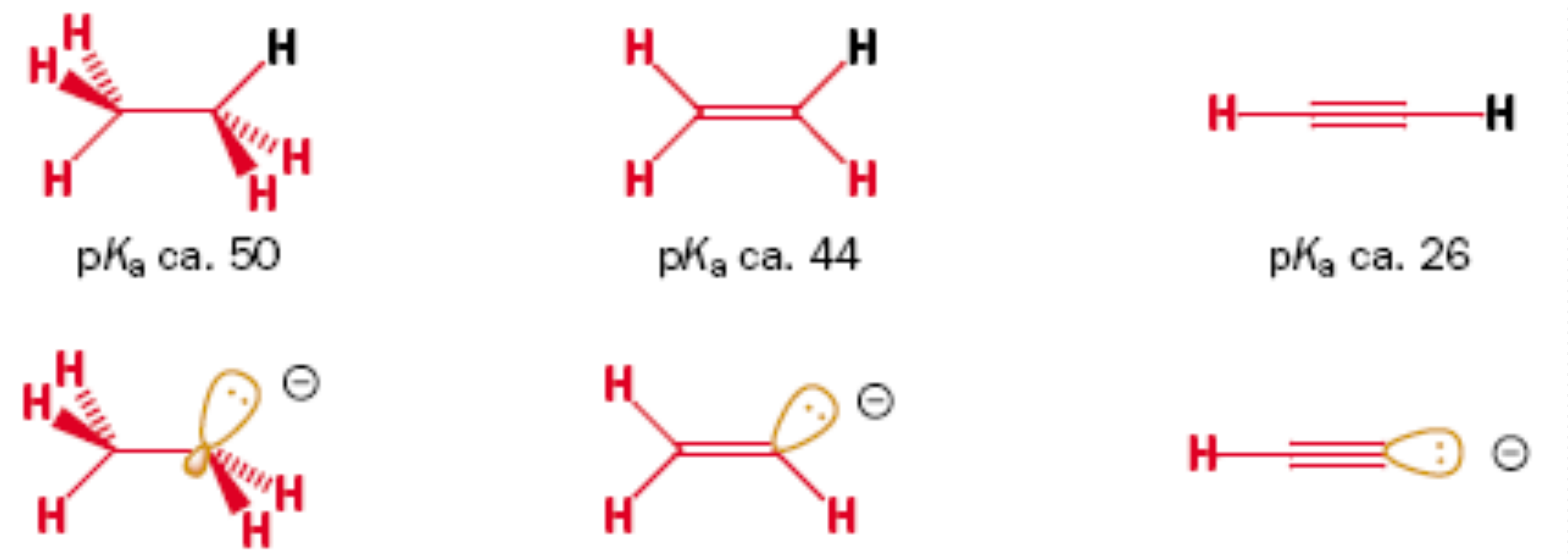
Substâncias aromáticas são planares e possuem número de elétrons $\pi = 4n + 2$, onde n = número inteiro.

Hibridação

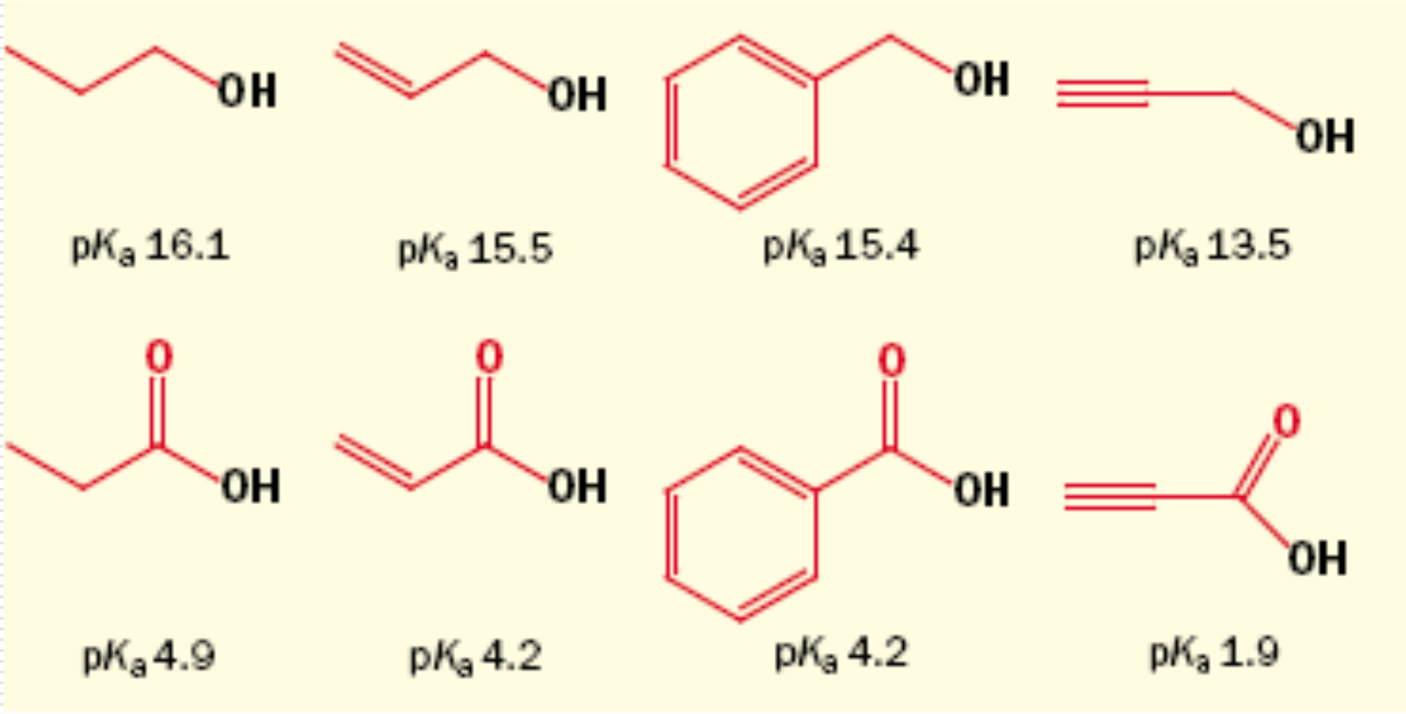


ESQUEMA 3.18 Hibridação e acidez de ligações C-H.

Caráter s do orbital com o par de eletróns

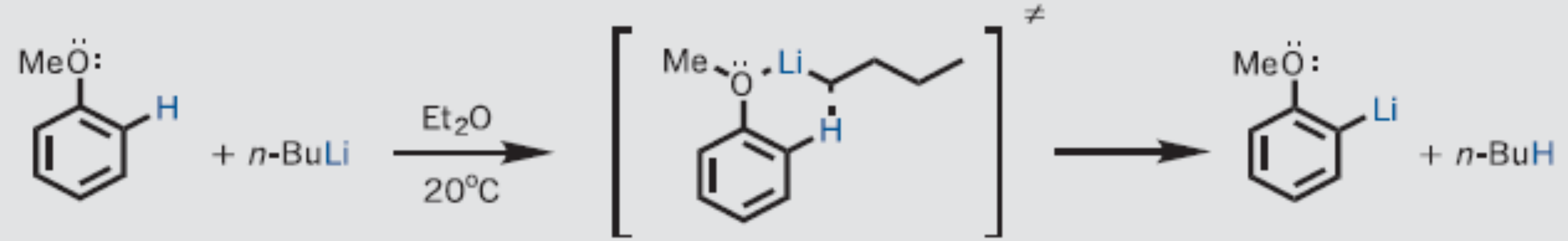


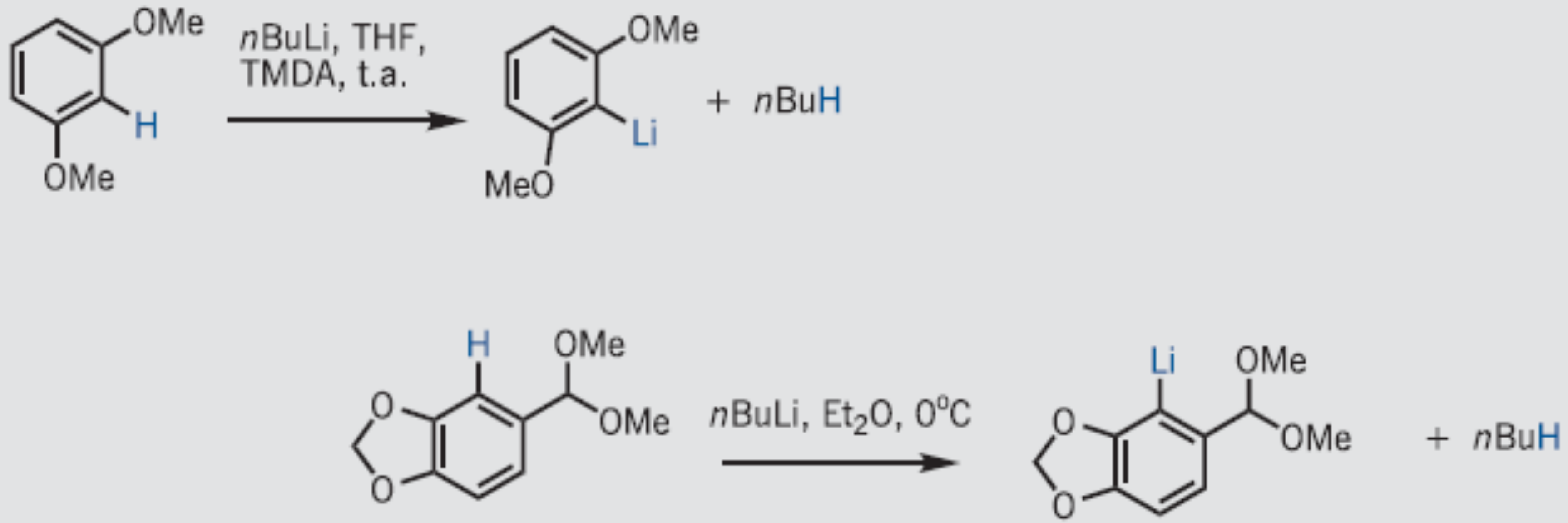
Hibridação nos grupos vizinhos também é importante

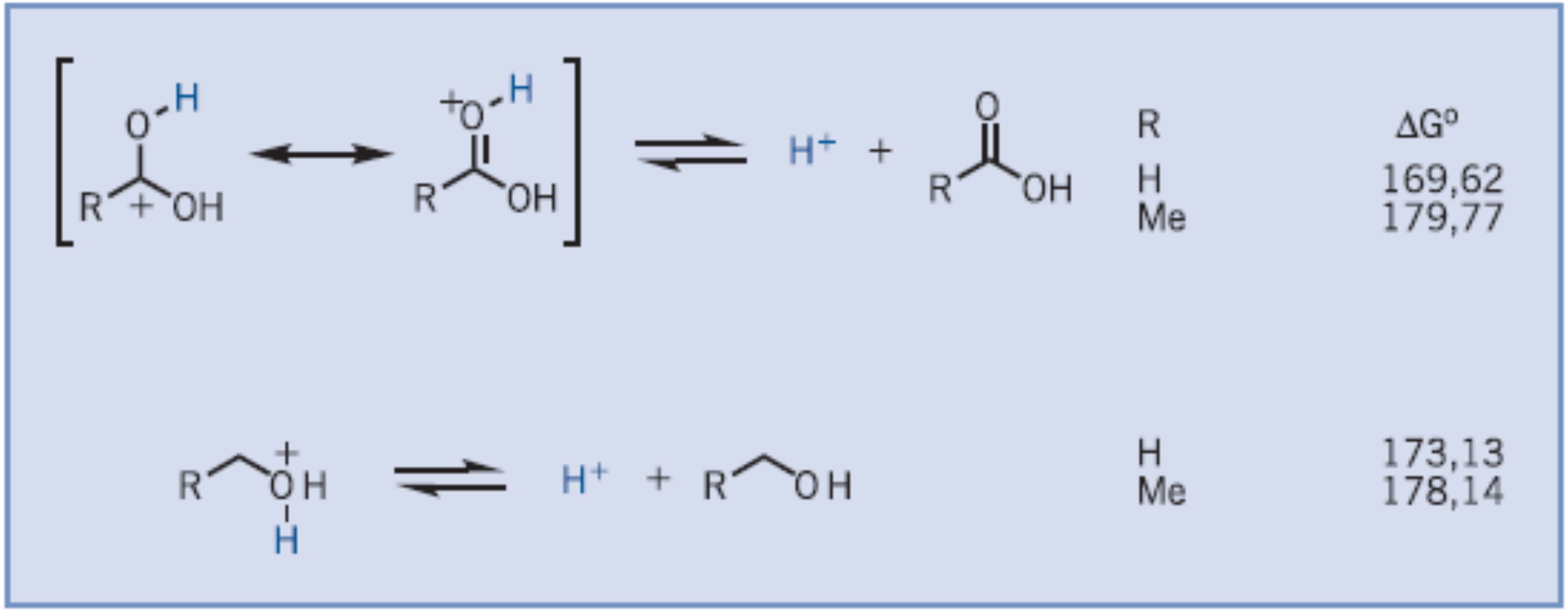


Maior caráter s no vizinho maior a eletronegatividade deste

Litiação de substâncias aromáticas







ESQUEMA 3.19 Dissociação de alcoóis e derivados carbonilados protonados em fase gasosa (Kcal/mol).

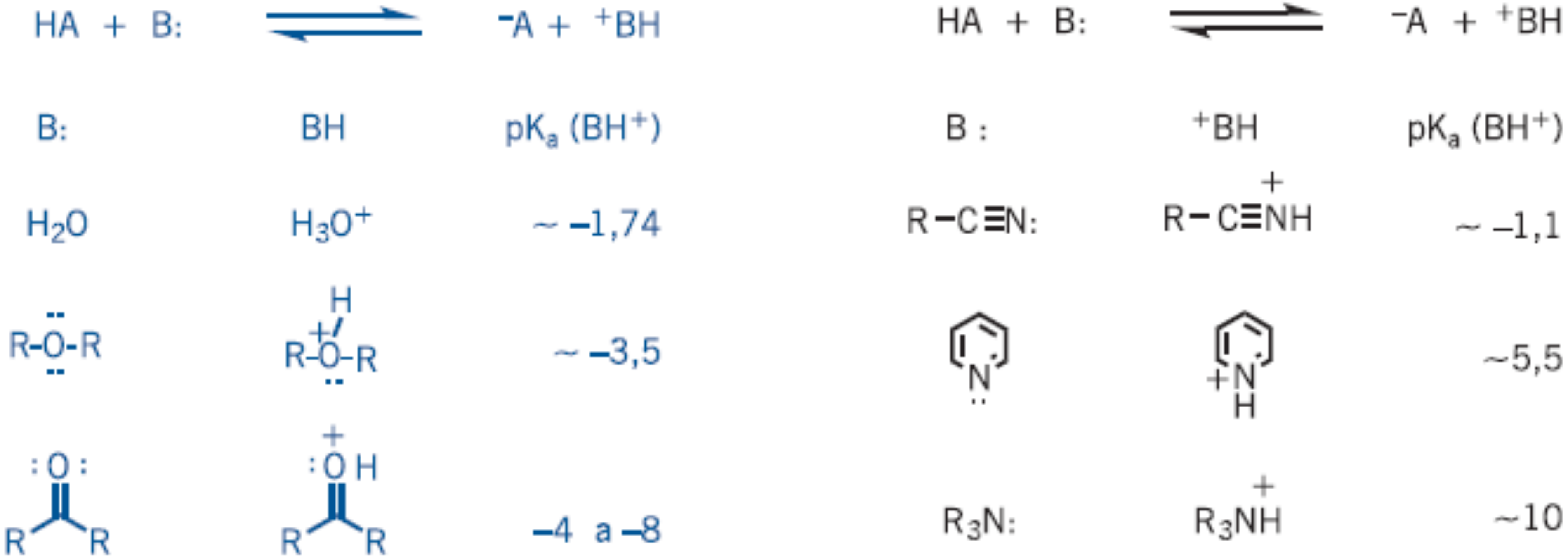
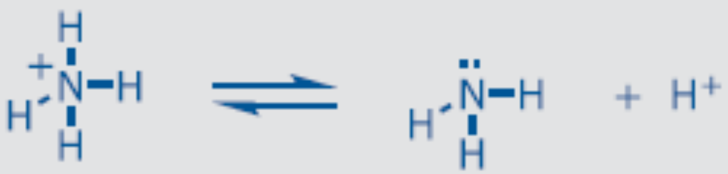


FIGURA 3.5 O efeito da hibridação na basicidade de derivados oxigenados e nitrogenados.

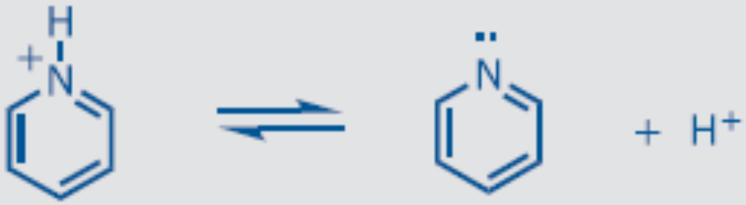
Piridina x NH_3

- Na fase gasosa piridina é mais básica que NH_3
- Contraria hibridização: Nsp^2 na piridina deveria ser menos básico do que o Nsp^3 no NH_3
- Cátion piridínio tem maior área superficial do que NH_4^+, tornando o íon mais estável
- Com o efeito do solvente → ordem se inverte → fatores entrópicos

(ΔG^o, ΔH^o e $T\Delta S^o$ em Kcal/mol e ΔS^o em cal/mol·K)



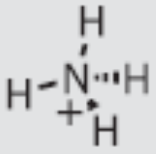
ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
195,7	204,0	27,8	8,3



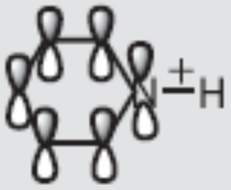
ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
214,7	222,0	24,5	7,3

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$	pK_a
12,6	12,4	+0,7	–0,2	9,24

ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$	pK_a
7,1	4,4	–9,1	–2,75	5,21



cátion mais solvatado,
4 átomos de H

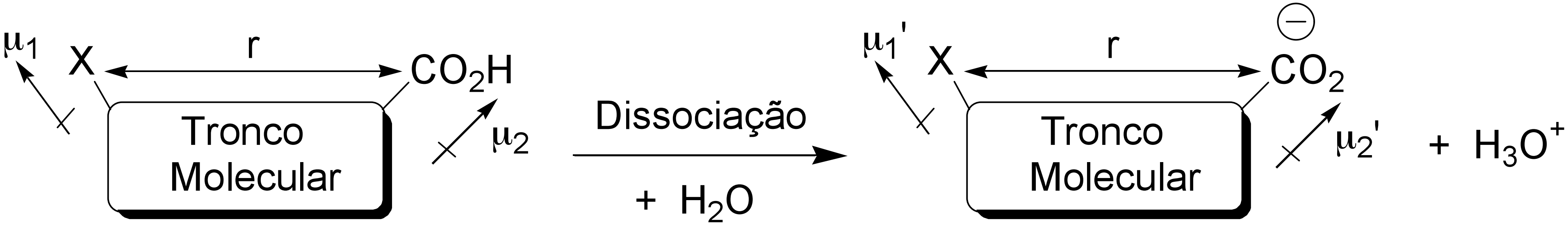


cátion menos solvatado,
1 átomo de H

Efeito Polar:
Efeito Indutivo x Efeito de Campo

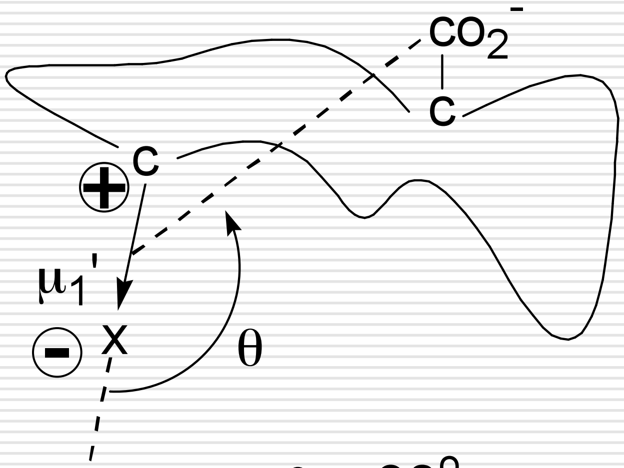
- Principais interações, em termos energéticos, são de natureza eletrostática
  - Carga-carga
  - Carga-dipolo (permanente)
  - Dipolo-Dipolo (permanente)
  - Ligação hidrogênio
  - Dipolo-Dipolo instantâneo
  - Dipolo instantâneo-Dipolo instantâneo (London)

Na dissociação de um ácido



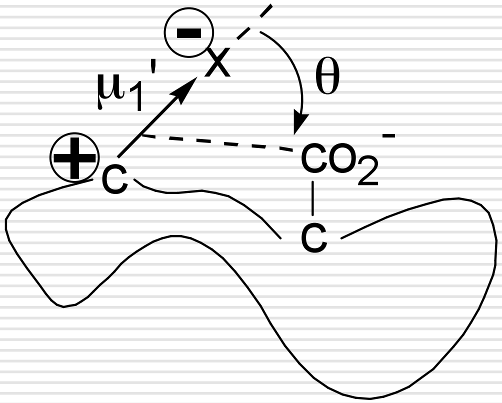
- ☐ Espécie não dissociada: dipolo-dipolo
- ☐ Ânion: carga-dipolo

Interação carga-dipolo no ânion



$\theta > 90^o$

$\cos\theta < 0$



$\theta < 90^o$

$\cos\theta > 0$

$$E_{c\arg a-dipolo} = (cte)x\frac{\mu.\cos\theta}{r}$$

Efeito indutivo? Não seria efeito de campo em átomos vizinhos?

- **Efeito indutivo**: seria transmitido através das ligações químicas
- **Efeito de campo**: transmitido através do espaço

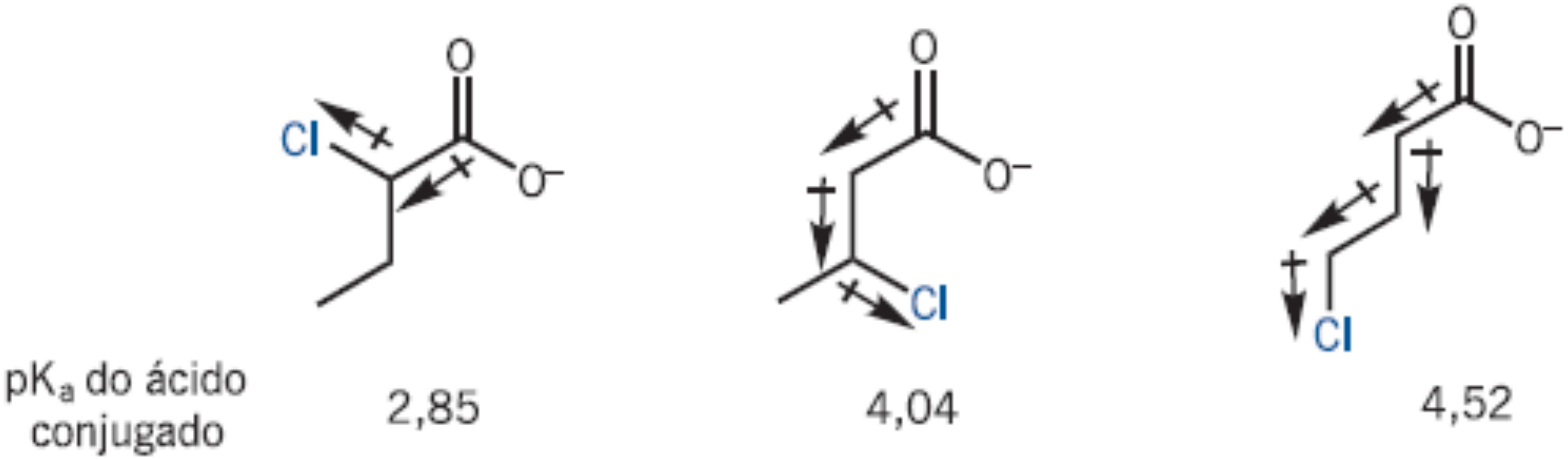
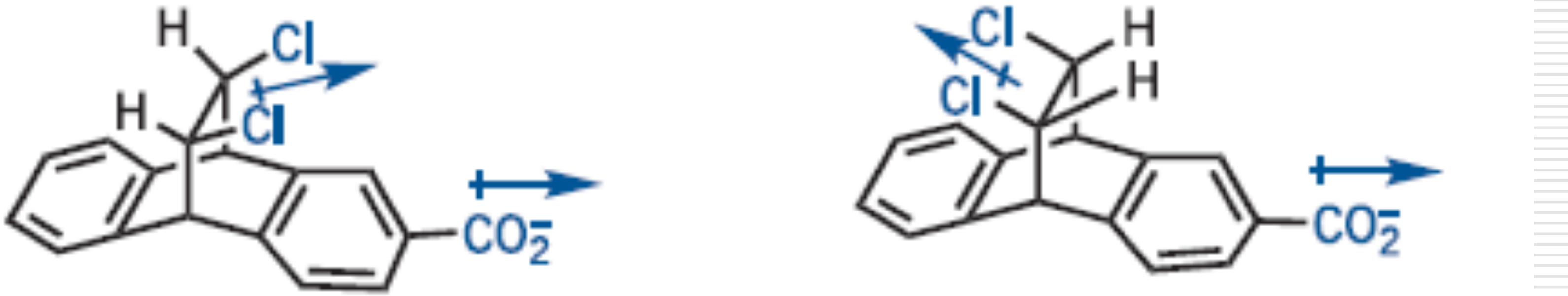


FIGURA 3.6 Efeito polar do cloro na dissociação (pK_a) de ácidos clorobutíricos isoméricos.

Efeito de campo



pK$_a$ (ácido conjugado) = 6,07

pK$_a$ (ácido conjugado) = 5,67

FIGURA 3.7 Efeito de campo na acidez de ácidos carboxílicos isoméricos.

Maior número de interações carga-dipolo estabiliza sistema

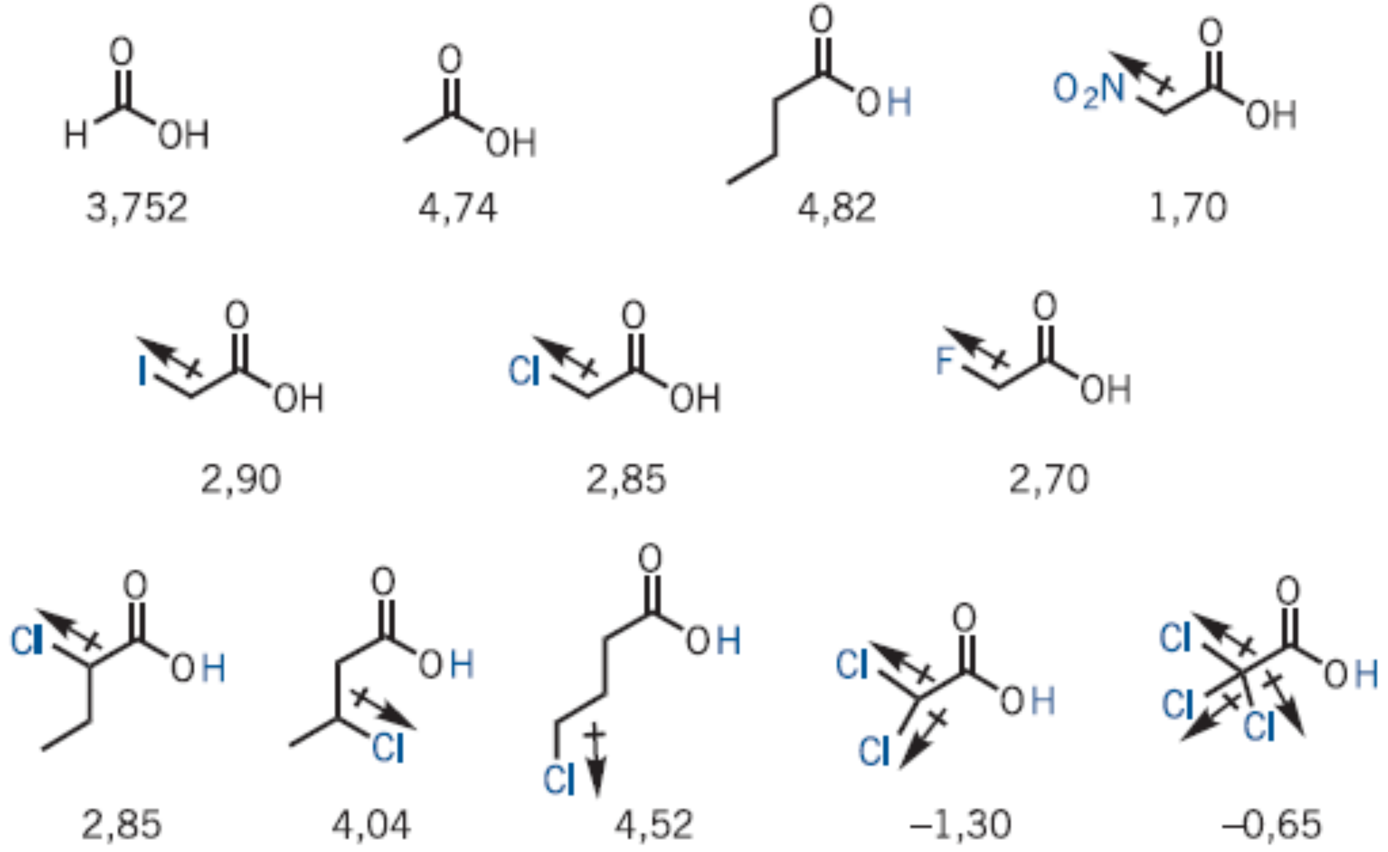
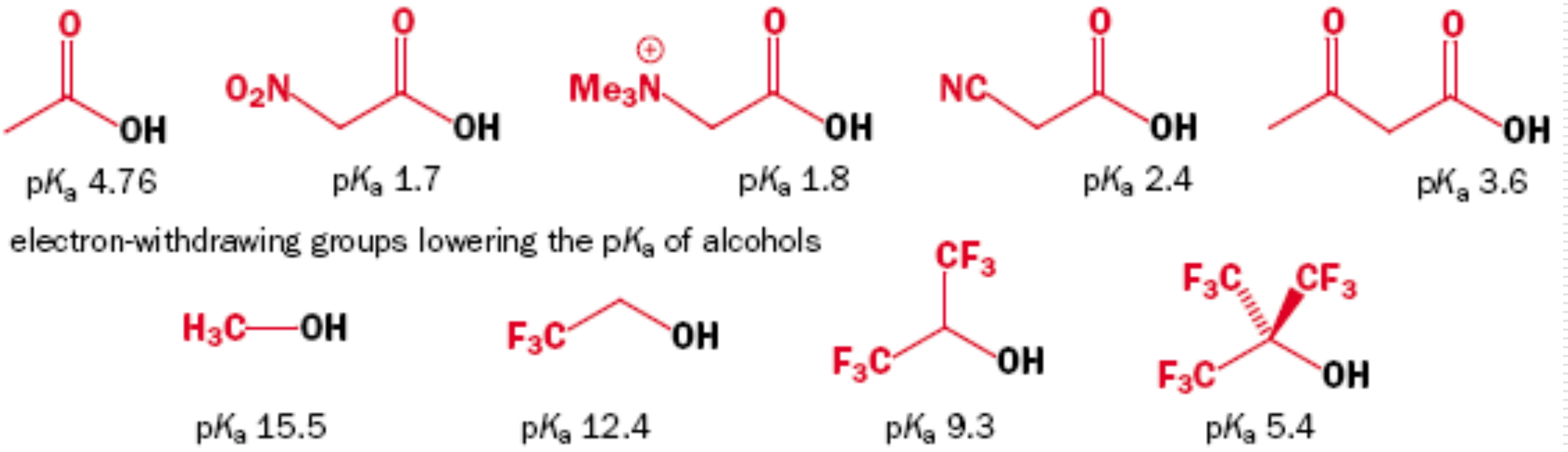
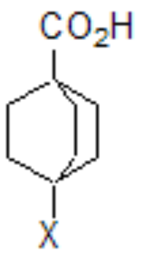
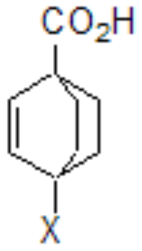
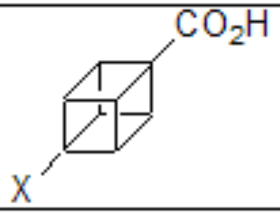
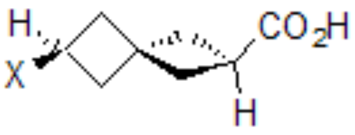
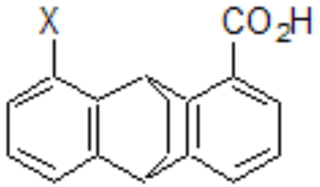
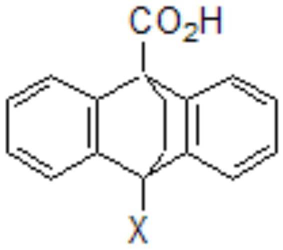
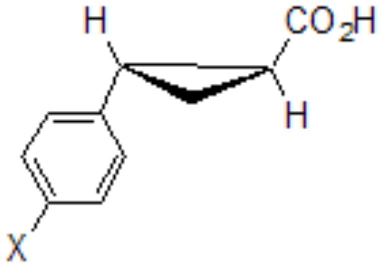
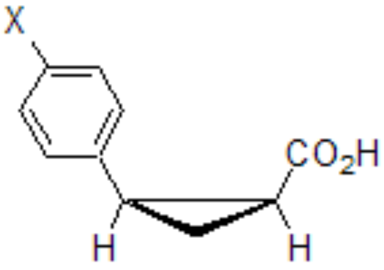


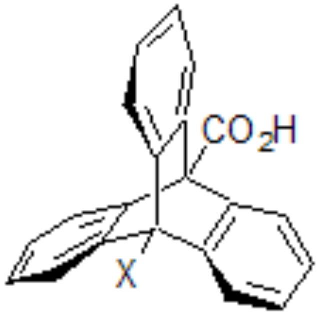
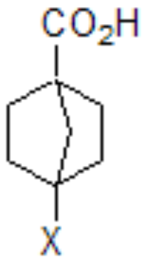
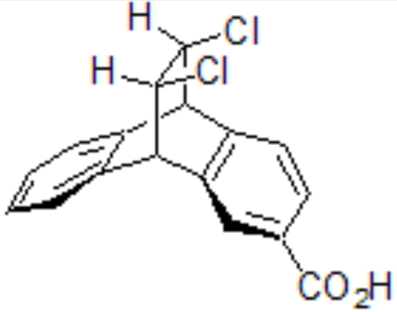
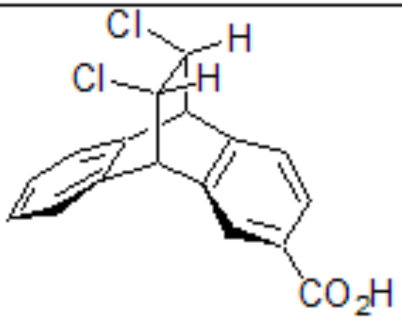
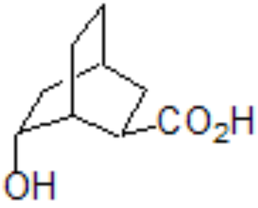
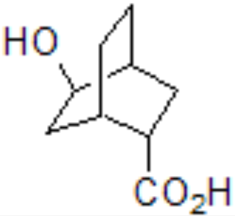
FIGURA 3.8 Valores de pK_a para ácidos carboxílicos halogenados.

Maior o dipolo maior a interação (estabilizante ou não) com a carga negativa



Molécula	pK$_a$ (EtOH/H$_2$O 50% p/p, 25°C)	Molécula	pK$_a$ (EtOH/H$_2$O 50% p/p, 25°C)
	X = H 6,87 X = CH_3 6,89 X = OCH_3 6,40 X = Cl 6,13 X = Br 6,14 X = CF_3 6,25 X = CN 5,85 X = NO_2 5,82 X = $N(CH_3)_3^+$ 5,37		X = H 6,54 X = CH_3 6,50 X = Cl 5,72 X = CF_3 5,79 X = CN 5,49 X = $N(CH_3)_3^+$ 4,84
	X = H 5,94 X = OCH_3 5,40 X = Br 5,32 X = CN 5,14		X = H 6,27 X = Br 5,93 X = CN 5,85
	X = H 5,99 X = CH_3 6,07 X = OCH_3 6,15 X = Cl 6,24 X = CN 6,05		X = H 5,75 X = CH_3 5,78 X = OCH_3 5,50 X = Cl 5,21 X = Br 5,21 X = CN 6,05 X = NO_2 5,21
	X = H 6,33 X = 4-CH_3 6,43 X = 4-OCH_3 6,40 X = 3-Cl 6,12 X = 4-Cl 6,22 X = 3-NO_2 5,96		X = H 5,78 X = 4-OCH_3 5,85 X = 3-Br 5,61 X = 4-Br 5,63 X = 3-NO_2 5,41 X = 4-NO_2 5,33

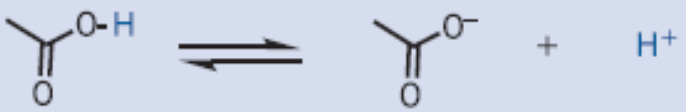
Efeito de campo (Continuação)

	X = H 5,20 X = CH_3 5,23 X = Cl 4,67 X = Br 4,67 X = NO_2 4,40		X = H 6,04 X = Br 5,39 X = CN 5,23 X = NO_2 4,55
	6,07		5,67
	6,42		6,47

[a] Stock, L. M. *J. Chem. Ed.* **1972**, *94(6)*, 400-404.

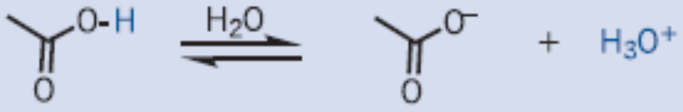
[b] Fuchs, R.; Kaplan, C. A.; Bloomfield, J. J.; Hatch, L. F. *J. Org. Chem.* **1962**, *27*, 733

dissociação em fase gasosa



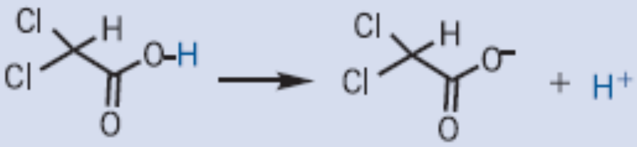
ΔGº	ΔHº	ΔSº	TΔSº
341,1	348,1	25,6	7,0

dissociação em água



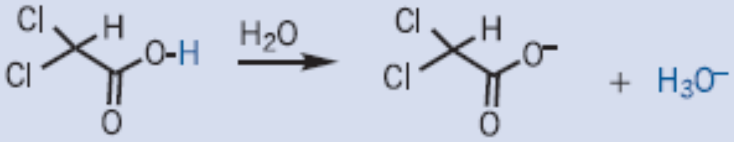
ΔGº	ΔHº	ΔSº	TΔSº	pK_a
6,5	–0,11	–22,0	–6,55	4,756

dissociação em fase gasosa



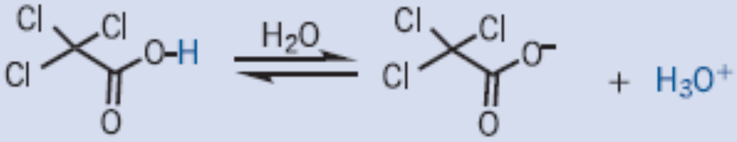
ΔGº	ΔHº	ΔSº	TΔSº
321,9	328,4	22,18	6,5

dissociação em água



ΔGº	ΔHº	ΔSº	TΔSº	pK_a
1,8	–6,1	–6,0	–1,78	1,3

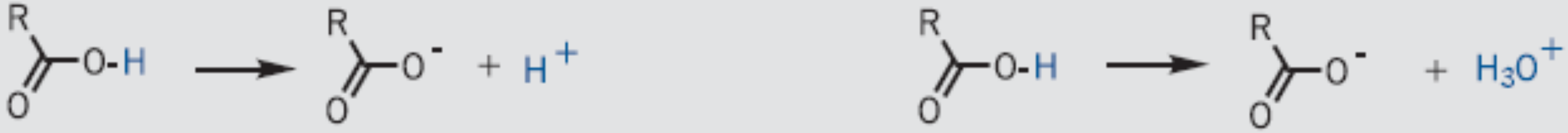
dissociação em água



ΔGº	ΔHº	ΔSº	TΔSº	pK_a
0,87	1,0	2,0	0,6	0,64

[ΔGº]= kcal/mol
[ΔHº]= kcal/mol
[ΔSº]= cal/mol.K
[TΔSº]= kcal/mol

Efeitos de grupos alquila na dissociação de derivados do ácido acético



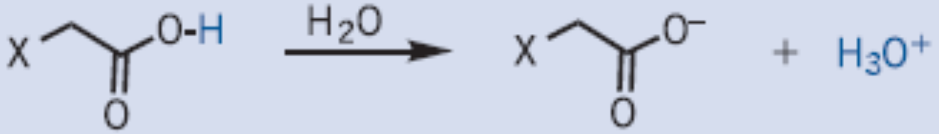
	ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
R = CH_3	341,1	348,1	23,5	7,0
R = CH_2CH_3	340,4	347,4	23,5	7,0
R = *t*Bu	337,6	344,6	23,5	7,0

	ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$	pK_a
R = CH_3	6,5	–0,11	–22,0	–6,55	4,75
R = CH_2CH_3	6,6	–0,23	–23,0	–6,83	4,87
R = *t*Bu	6,9	–0,72	25,0	–7,62	5,03

ΔG^o, ΔH^o e $T\Delta S^o$ em Kcal/mol e ΔS^o em cal/mol·K

- Solvatação inverte ordem intrínseca
- Acidez dominado pelo termo entrópico

Efeitos de substituintes na dissociação de derivados do ácido acético

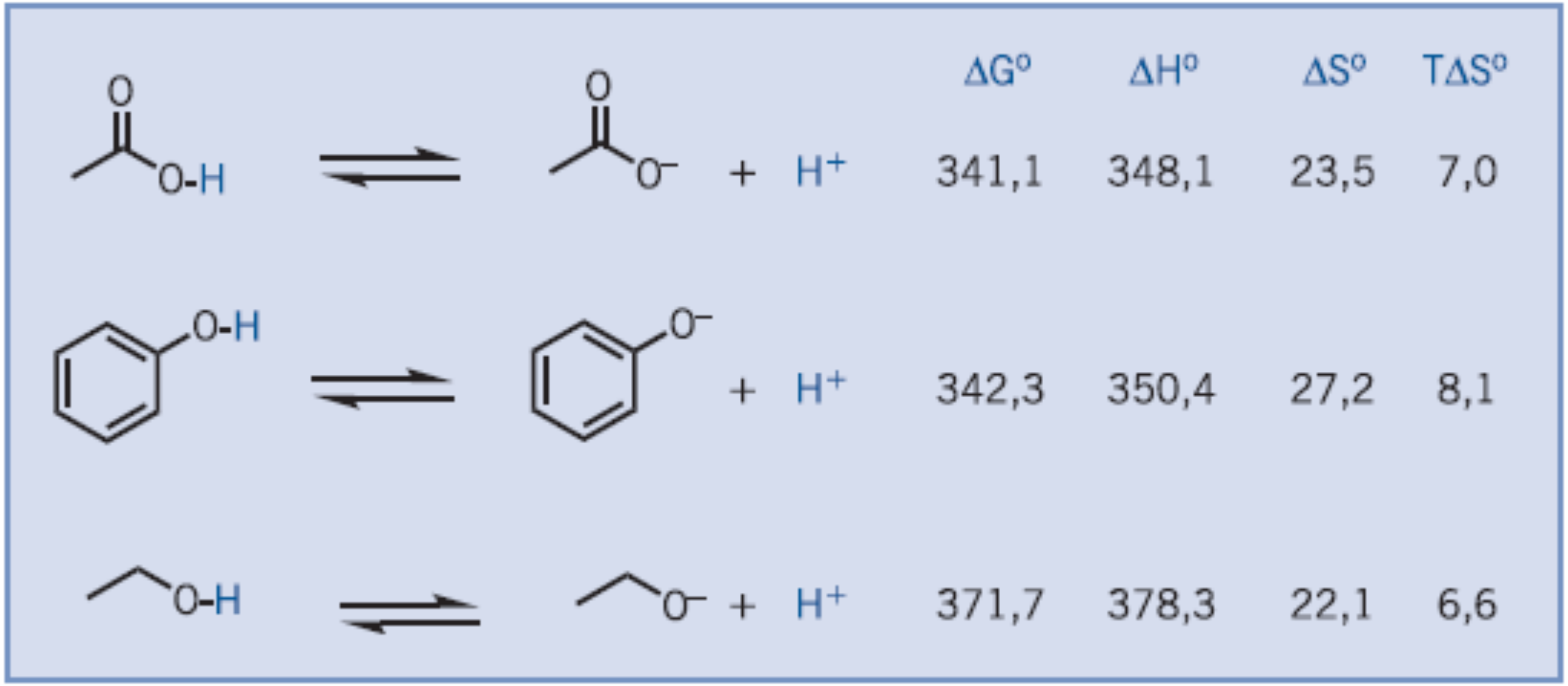


X	pK_a (H_2O)
F	2,70
Cl	2,85
I	2,90

	ΔG°	ΔH°	ΔS°	TΔS°
X = F	331,6	339,1	25,2	7,5
X = Cl	329,0	336,5	25,2	7,5
X = Br	328,2	334,8	22,1	6,6
X = I	327,7	334,7	23,5	7,0

ESQUEMA 3.21 Dissociações de ácidos carboxílicos halogenados em fase gasosa e pK_a.

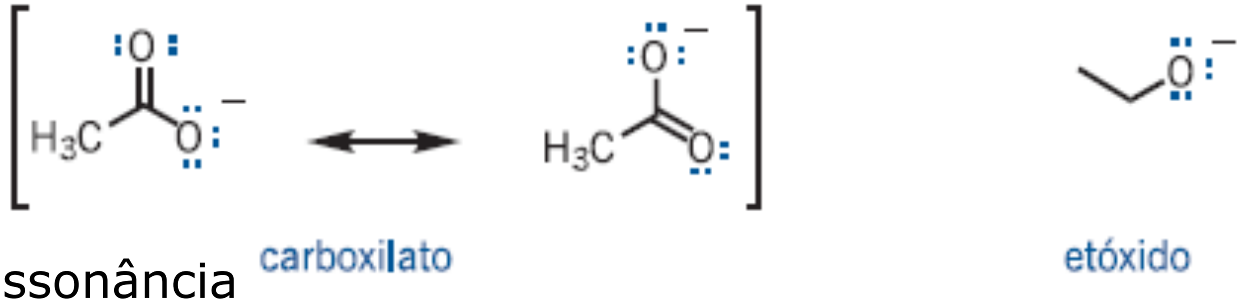
Efeito de ressonância



ΔG^o	ΔH^o	ΔS^o	$T\Delta S^o$
341,1	348,1	23,5	7,0
342,3	350,4	27,2	8,1
371,7	378,3	22,1	6,6

ESQUEMA 3.22 Dissociações em fase gasosa do ácido acético, fenol e etanol (ΔG^o, ΔH^o e $T\Delta S^o$ em Kcal/mol e ΔS^o em cal/mol·K).

Efeito de ressonância (cont.)



2 estruturas ressonância

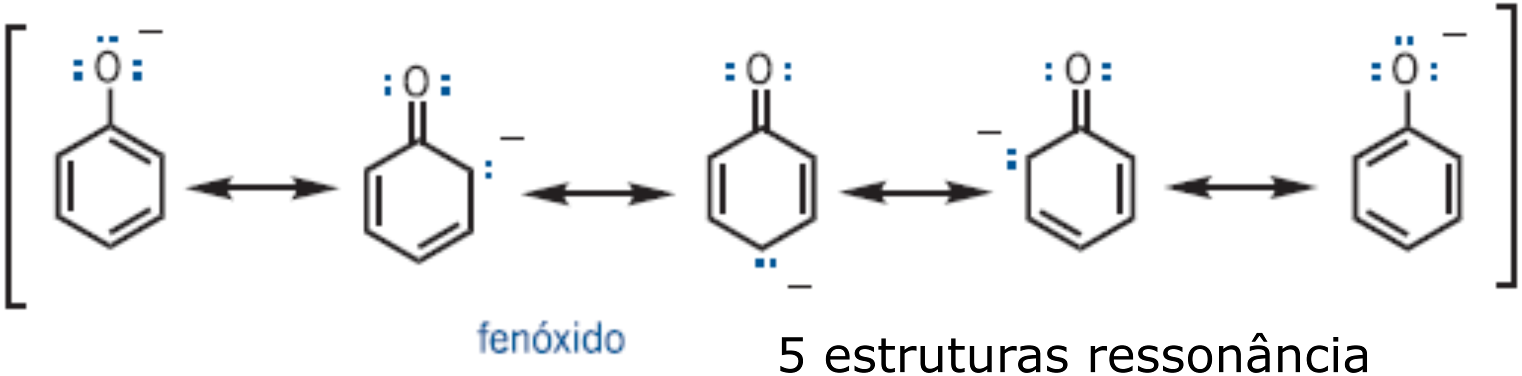
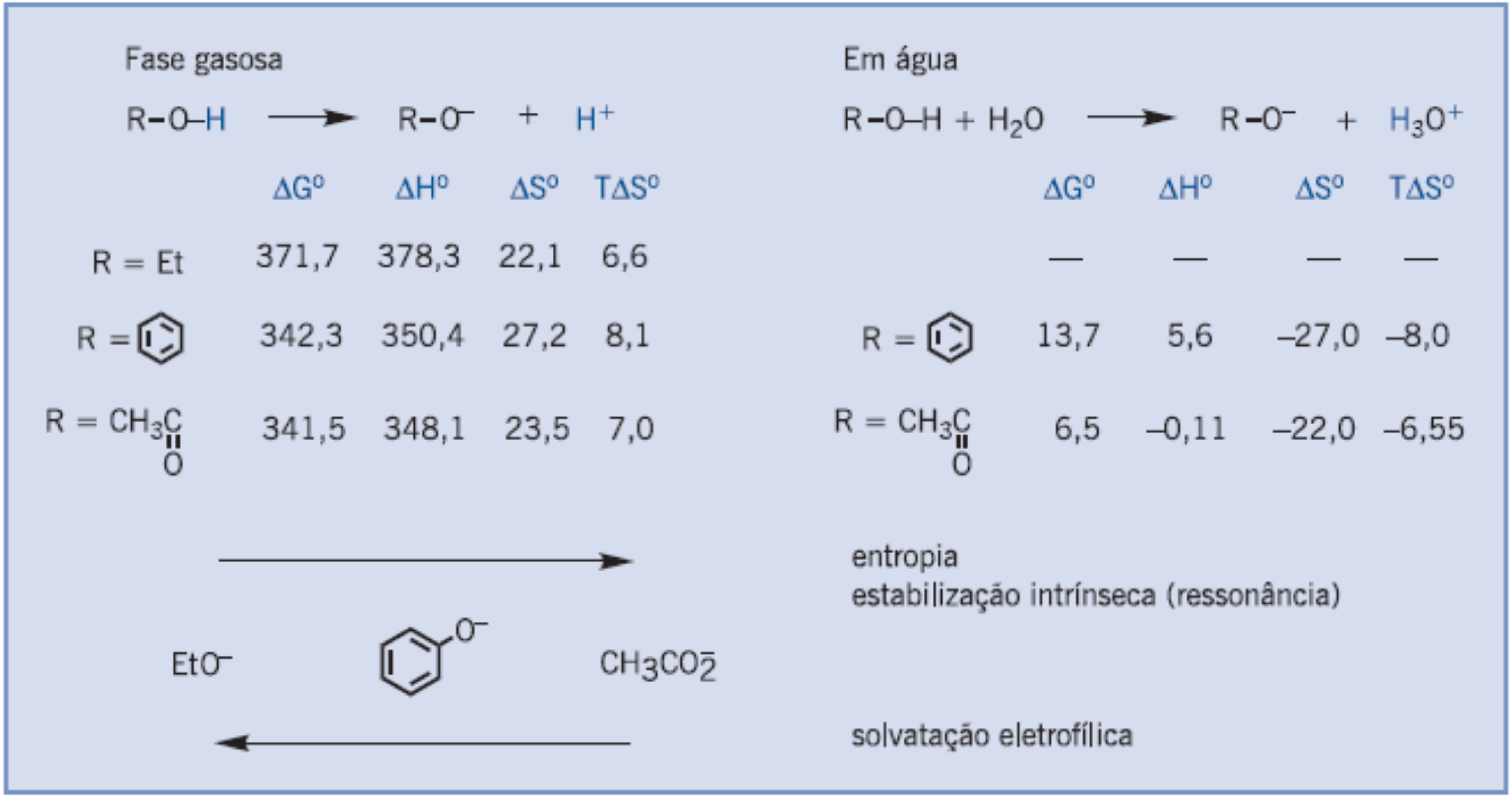


FIGURA 3.9 Estruturas canônicas no acetato e no fenolato.

5 estruturas ressonância

Intrínseco x solução aquosa: dominada por efeitos entálpicos



Fase gasosa

$R{-}O{-}H \longrightarrow R{-}O^- + H^+$

	ΔG°	ΔH°	ΔS°	TΔS°
R = Et	371,7	378,3	22,1	6,6
R = ⌬	342,3	350,4	27,2	8,1
R = $\underset{\underset{O}{\|}}{CH_3C}$	341,5	348,1	23,5	7,0

Em água

$R{-}O{-}H + H_2O \longrightarrow R{-}O^- + H_3O^+$

	ΔG°	ΔH°	ΔS°	TΔS°
	—	—	—	—
R = ⌬	13,7	5,6	–27,0	–8,0
R = $\underset{\underset{O}{\|}}{CH_3C}$	6,5	–0,11	–22,0	–6,55

entropia
estabilização intrínseca (ressonância)

EtO^- $CH_3CO_2^-$

solvatação eletrofílica

ESQUEMA 3.23 Dissociações em fase gasosa e em água para o etanol, fenol e ácido acético (ΔG°, ΔH° e TΔS° em Kcal/mol e ΔS° em cal/mol·K).

Resumo

- Propriedades ácido-base de funções químicas diferentes costumam ser dominadas pelo termo entálpico, que é fortemente influenciado pelo fator intrínseco à estrutura molecular

- Se a função for a mesma, os fatores entrópicos podem (e usualmente são) os fator que controla a posição do equilíbrio

Ligações C-H ácidas: ressonância em acão

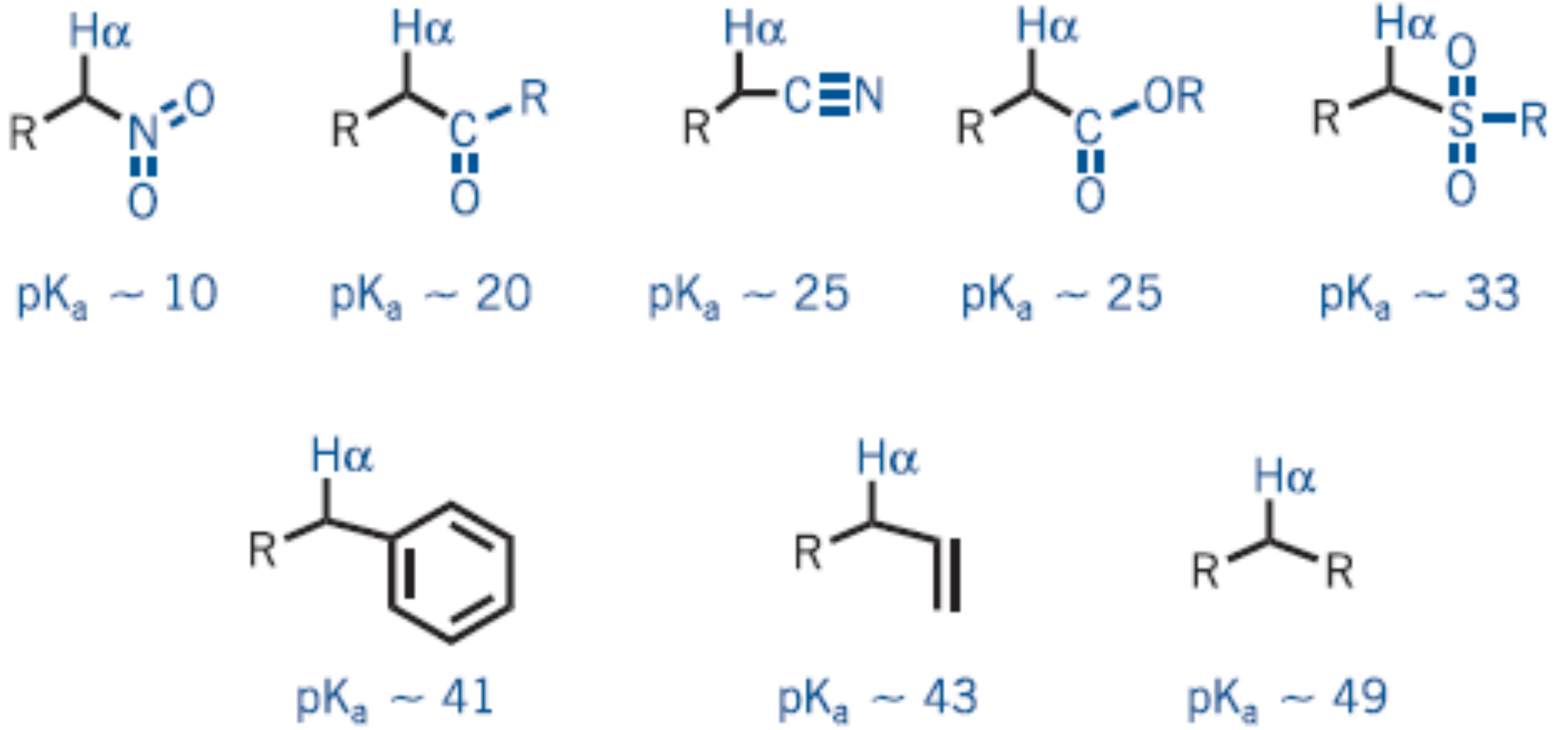
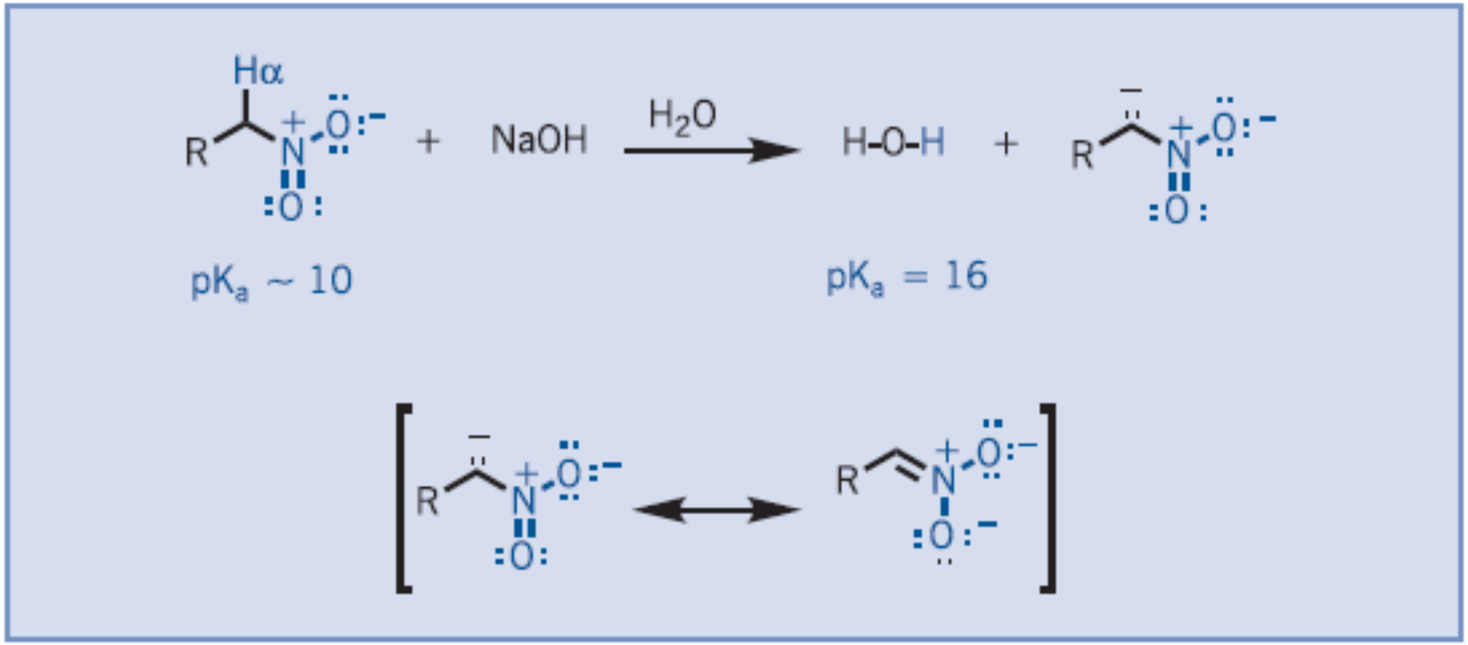
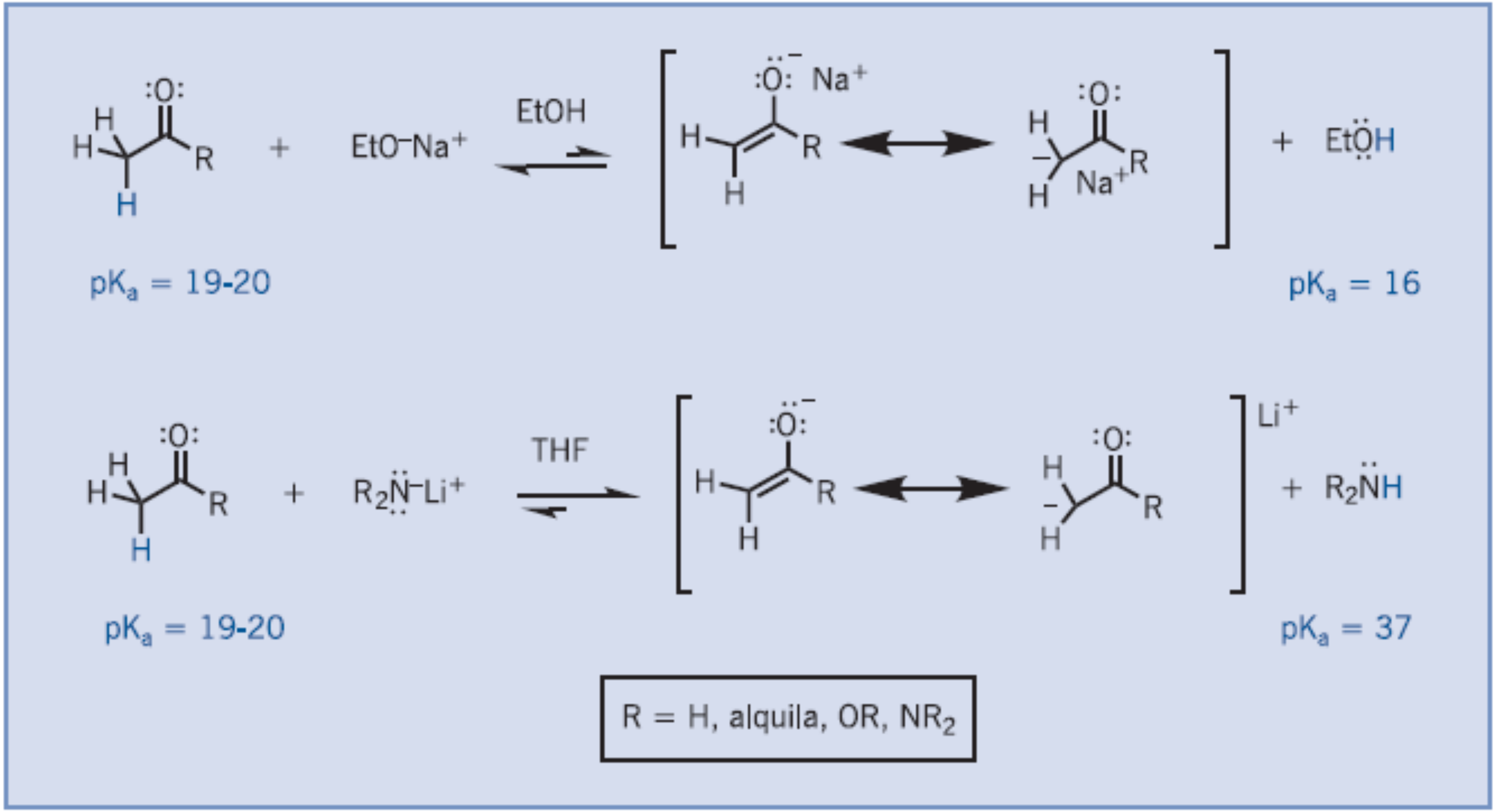


FIGURA 3.10 Efeito do substituinte na acidez (pK_a em água) de ligações C-H.



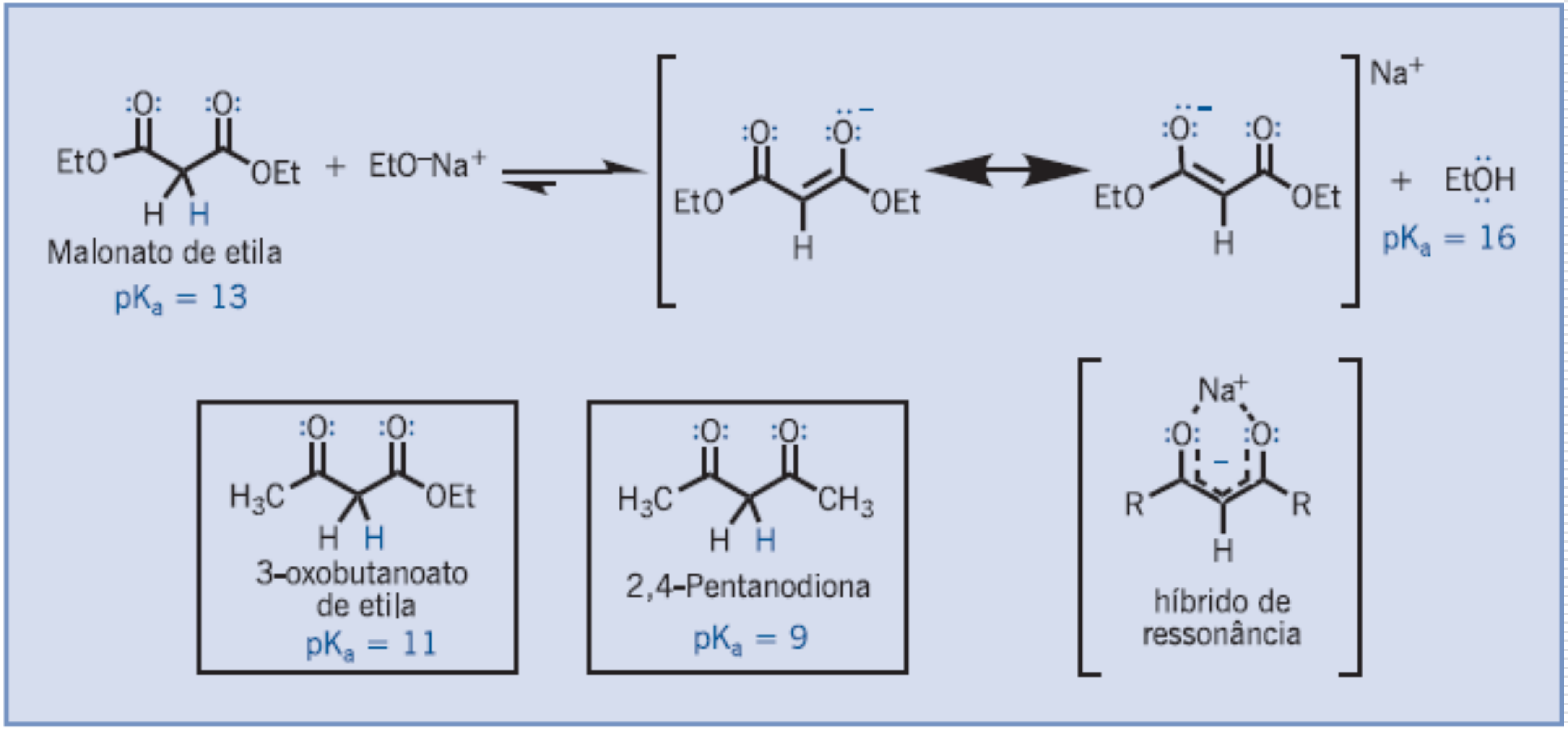
ESQUEMA 3.24 Dissociação de nitroalcanos.

Formação de enolatos



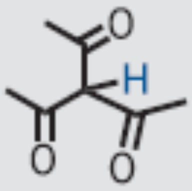
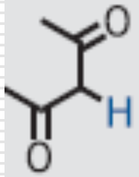
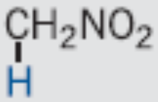
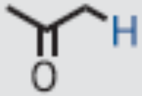
ESQUEMA 3.25 Dissociação de derivados carbonilados: a força da base e a posição do equilíbrio.

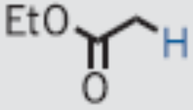
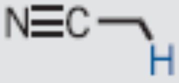
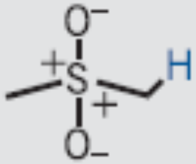
Efeito de mais de uma conjugação

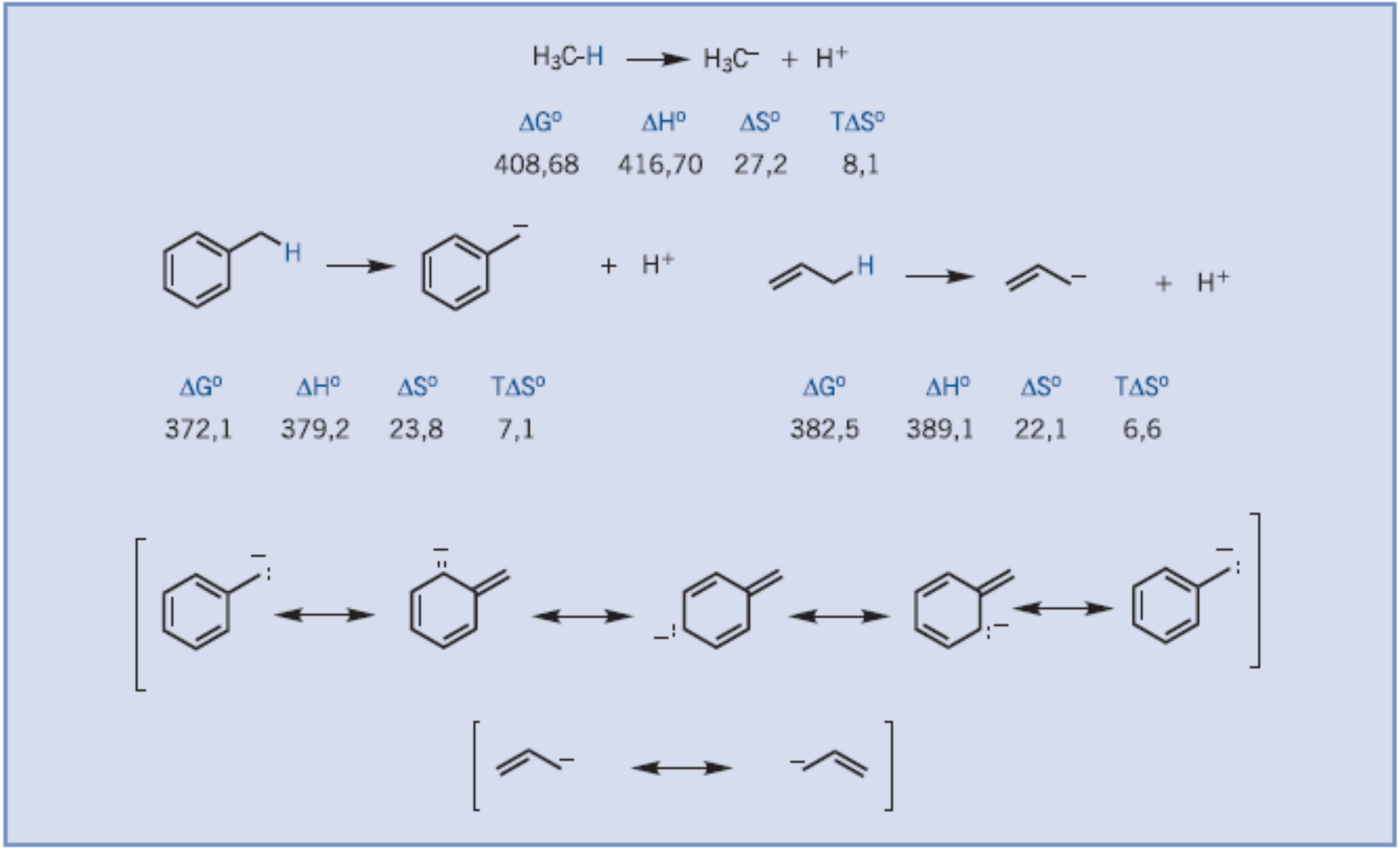


ESQUEMA 3.26 Dissociações do malonato de etila, acetoacetato de etila e β-dicetona.

Dissociação de ligações C-H em água e em DMSO

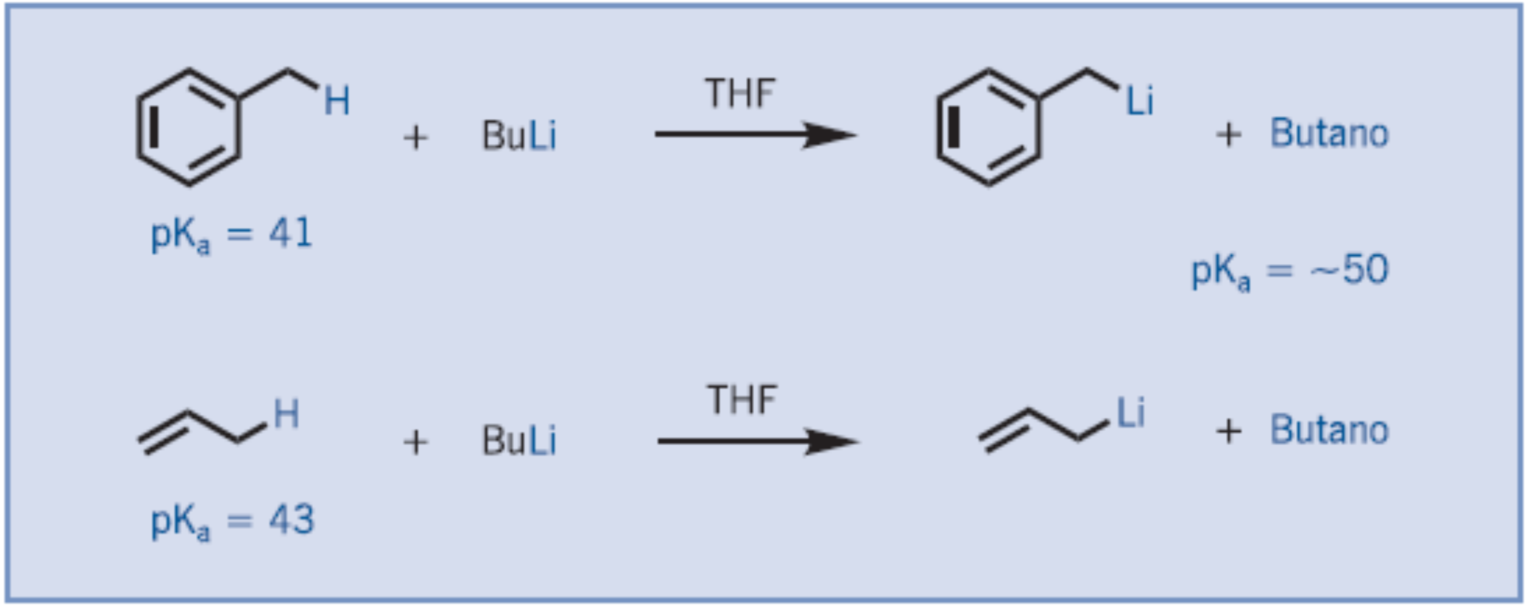
	pK_a (H_2O)	pK_a (DMSO)
	6,0	8,60
	9,0	13,33
 $\underset{H}{CH_2}NO_2$	11,0	17,3
	20,0	26,4

	pK_a (H_2O)	pK_a (DMSO)
	24,5	
	31,0	31,3
	31,0	



ESQUEMA 3.27 Dissociações de hidrocarbonetos em fase gasosa: a estabilização de ânions benzílicos e alílicos (ΔG°, ΔH° e TΔS° em Kcal/mol e ΔS° em cal/mol·K).

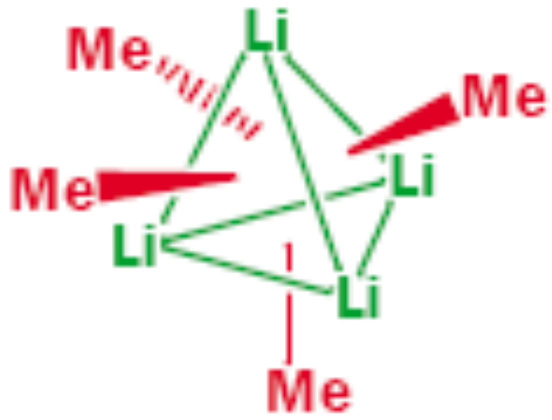
Gerando carbânions em solução



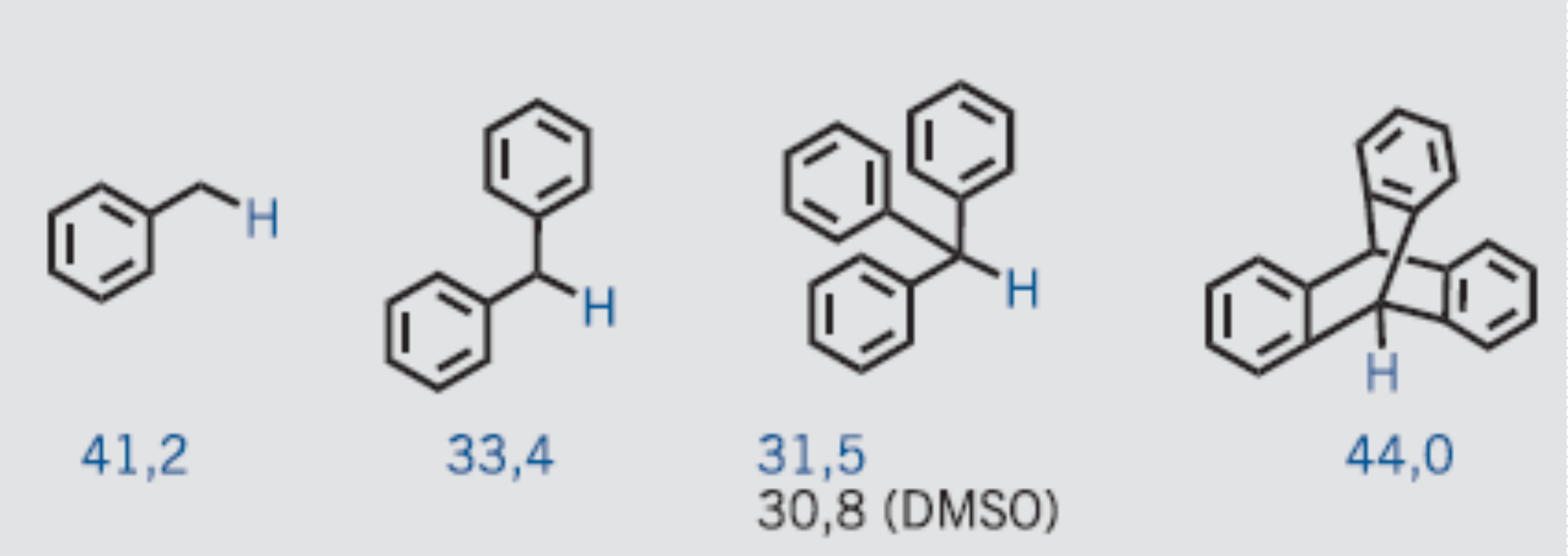
ESQUEMA 3.28 Dissociação de ligações alílicas e benzílicas promovidas por amidetos de lítio em meio apolar anidro.

Organolítio usualmente se encontram sob a forma de aglomerados

- Tetrâmeros
- Hexâmeros
- Octâmeros
- etc



Como explicar os valores de pKa?



Métodos de medida de acidez e basicidade na fase gasosa

Afinidades Protônicas

$M + H^+ \rightarrow MH^+$ $\Delta H_{reação} = -AP$

onde,

$\Delta_f H^o(MH^+) = \Delta_f H_o(M) + \Delta_f H_o(H^+) - AP$

Ciclo termodinâmico para obter a Afinidade Protônica (*AP*) de A$^-$

$$\mathrm{H{-}A} \longrightarrow \mathrm{H}^{\bullet} + \mathrm{A}^{\bullet} \qquad D_{HA}$$

$$\mathrm{A}^{\bullet} + e^{\ominus} \longrightarrow \mathrm{A}^{\ominus} \qquad -AE_{A}$$

$$\mathrm{H}^{\bullet} \longrightarrow \mathrm{H}^{\oplus} + \mathrm{A}^{\ominus} \qquad PI_{H} = 315{,}1 \text{ kcal/mol}$$

$$\mathrm{H{-}A} \longrightarrow \mathrm{H}^{\oplus} + \mathrm{A}^{\ominus}$$

$$AP = DH_{A} - AE_{A} + PI_{H}$$

Medindo-se as concentrações, mede-se K_{eq}

$$\mathbf{MH^+ + B \rightarrow M + BH^+}$$

$$K_{eq} = \frac{[M][BH^+]}{[MH^+][B]}$$

Técnicas que medem concentrações

- Espectroscopia
  - UV-Vis
  - RMN
  - IR
  - FT-ICR
  - ESCA
  - XPS
  - etc

Tendo-se

$$-RT\ \ln K_{eq} = \Delta G = \Delta H - T\Delta S$$

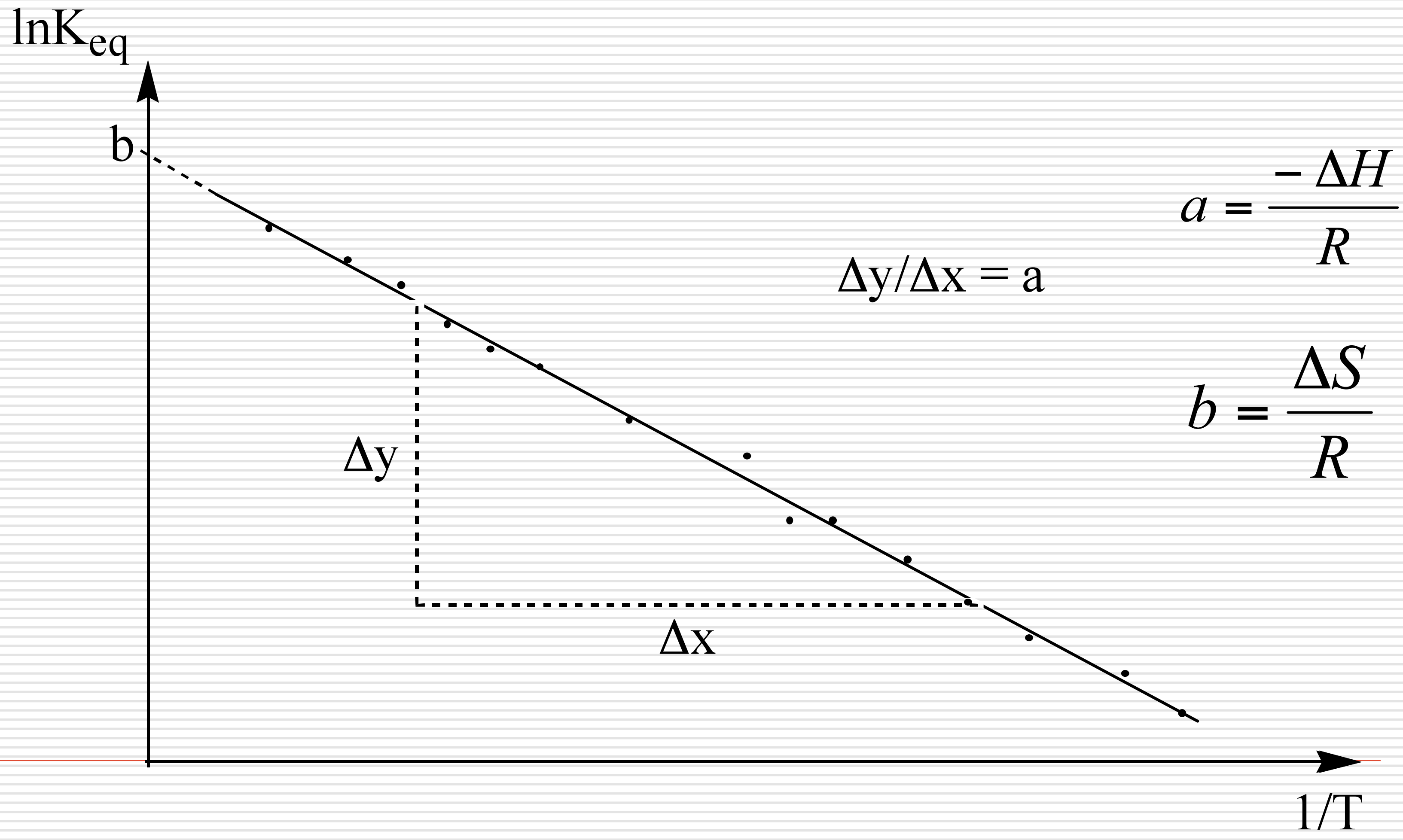
Dividindo
por
-RT

$$-RT\ \ln K_{eq} = \Delta H - T\Delta S$$

$$\underbrace{\ln K_{eq}}\ = \underbrace{\frac{\Delta H}{R}} \times \underbrace{\left(\frac{1}{T}\right)} + \underbrace{\frac{\Delta S}{R}}$$

$$\boldsymbol{y} = \boldsymbol{a}\ .\ \boldsymbol{x} + \boldsymbol{b}$$

Gráfico de van't Hoff usado para determinar ΔH, ΔG e ΔS de equilíbrios químicos.



$$\Delta y / \Delta x = a$$

$$a = \frac{-\Delta H}{R}$$

$$b = \frac{\Delta S}{R}$$

Protonação de H_2

$$H_2 \quad + \quad H^+ \quad \rightarrow \quad H_3^+$$

$$\Delta_f H^o(H_3^+) = \Delta_f H^o(H_2) + \Delta_f H^o(H^+) - AP$$

$\Delta_f H^o(H_2)$ = 0 kcal/mol (pela definição de entalpia de formação)
$AP(H_2)$ = 100,9 kcal/mol
$\Delta_f H^o(H^+)$ = 365,7 kcal/mol (pela convenção do íon),

$$\Delta_f H^o(H_3^+) = 0 + 365{,}7 - 100{,}9 = 264{,}8 \text{ kcal/mol}$$

Usando $\Delta_f H^o(H_3^+)$ para calcular $\Delta_f H^o(CH_5^+)$

$H_2 + H^+ \rightarrow H_3^+ \qquad (\Delta H_{reação})_1 = -AP(H_2)$

e

$H_3^+ + CH_4 \rightarrow H_2 + CH_5^+ \qquad (\Delta H_{reação})_2$

Temos

$CH_4 + H^+ \rightarrow CH_5^+ \qquad (\Delta H_{reação})_3 = -AP(CH_4)$

$(\Delta H_{reação})_3 = (\Delta H_{reação})_1 + (\Delta H_{reação})_2 = -AP(H_2) + (\Delta H_{reação})_2$

$AP(CH_4) = -(\Delta H_{reação})_3 = AP(H_2) - (\Delta H_{reação})_2$

- Assim, todas os dados de basicidade e afinidades por próton de qualquer molécula podem ser medidas de maneira similar

webbook.nist.gov/chemistry

Medindo pK_a

Titulação Ácido-Base

- Henderson-Hasselbalch

$$pK_a = pH - \log\frac{[A^-]}{[HA]}$$

[A-] = [HA] → [A-]/[HA] = 1 → log[A-] / [HA] = 0

Assim,

pKa = pH – 0
pKa = pH

Aspectos práticos

- menos útil do que usualmente possa parecer
  - nem sempre se tem quantidade suficiente de amostra de material altamente puro (~100mg)
  - material nem sempre é solúvel em água

Espectroscopia no Ultravioleta-Visível

- ☐ Determina-se as concentrações do ácido e sua base conjugada em um dado pH
- ☐ Lei de Lambert-Beer: $a_X = \varepsilon d[X]$
- ☐ $0.1 < [A-]/[HA] < 10$

$$pK_a = pH - \log\left(\frac{|a_{ion} - a|}{|a - a_{HA}|}\right)$$

Método da Solubilidade

- Solubilidade x pH (obtido com tampão)
- Titulação até que que ácido ou base conjugada precipite
- Obtém-se concentrações pelo K_{ps}

$$pK_a = pH - \log\left(\frac{S'}{S} - 1\right)$$

- S = Solubilidade da forma neutra
- S′ = solubilidade aparente, ou seja, da forma neutra + a ionizada

Método da Partição

- Sistema bifásico: Ex. Octanol/água
- Coeficiente de partição medido em diferentes pH's (tampão)
- Para ácidos:

$$pK_a = pH - \log\left(\frac{P}{P'} - 1\right)$$

- P = Coeficiente de partição da forma neutra
- P' = Coeficiente de partição aparente, ou seja, da forma neutra + a ionizada

Grau de dissociação

$$\%ionizado = \frac{100}{1 + 10^{(pK_a - pH)}}$$

Exemplo

- Um ácido tem pKa = 5,2. Qual o percentual do ácido que está ionizado em pH 6,0?
- O percentrual de ionização de um ácido é dado pela equação acima. Assim, em pH=6,

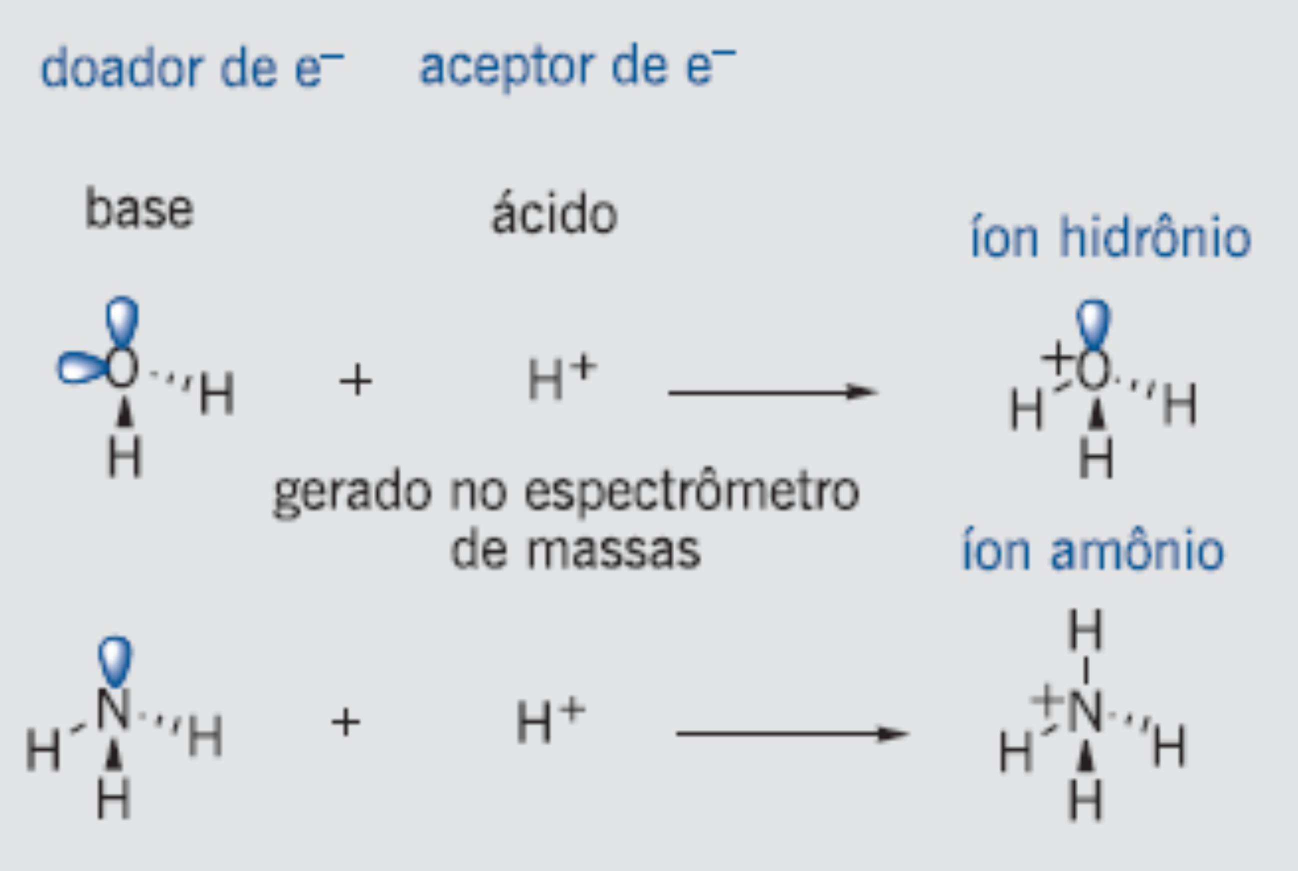
$$\%ionizado = \frac{100}{1+10^{(5,2-6,0)}} = \frac{100}{1+0,585}$$

$$\%ionizado = 86,3\%$$

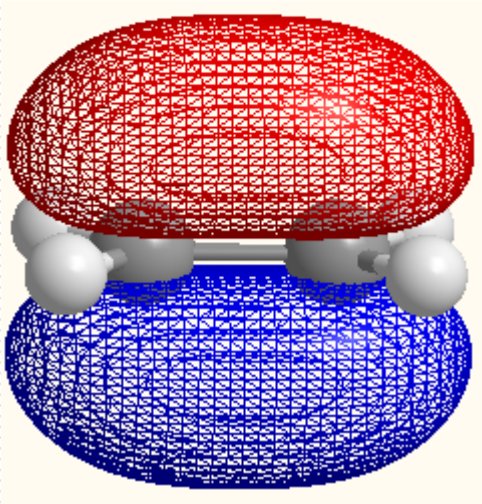
Tipos de Bases

n π σ

Bases n: Espécies com um par de elétrons isolado



Bases π: Espécies com um par de elétrons em uma ligação π



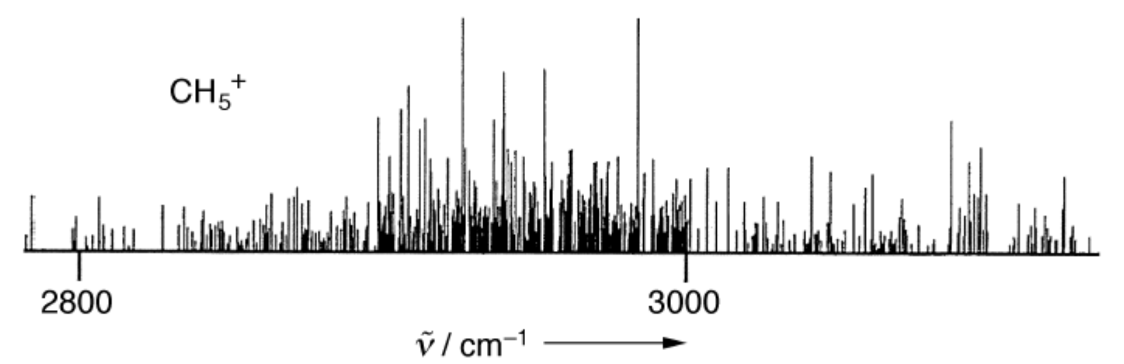
Bases σ: Espécies com um par de elétrons em uma ligação σ

CH_5^+: Resultante da protonação CH_4

$$CH_4 + e\,(h\nu) \rightarrow CH_4^{+\cdot} + 2\,e\,(h\nu')$$
$$CH_4^{+\cdot} + CH_4 \rightarrow CH_5^{+} + CH_3\cdot$$

CH_5^+: Resultante da reação de H_2 com CH_3^+

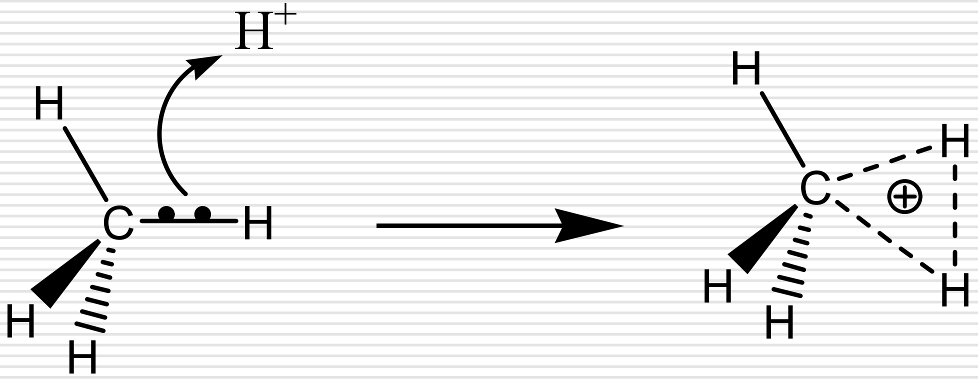
$$CD_4 + H^+ \rightarrow CD_4H^+ \rightarrow CD_2H^+ + HD$$
$$CD_3^+ + H_2 \rightarrow CD_3H_2^+ \rightarrow CDH_2^+ + D_2$$

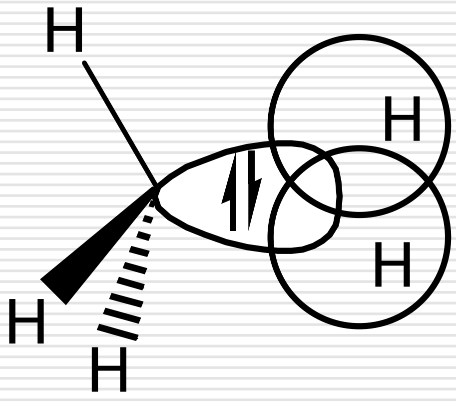


Espectro de IV de alta resolução do CH_5^+

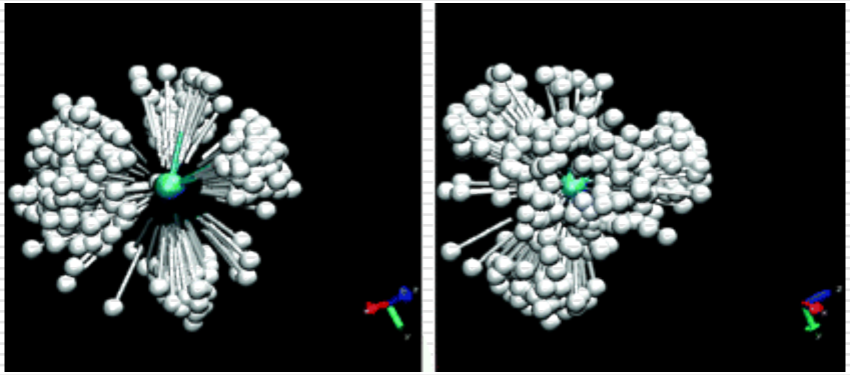
Oka, Tang and White, Science 1999,284, 135-137

Íon carbônio: Metano protonado





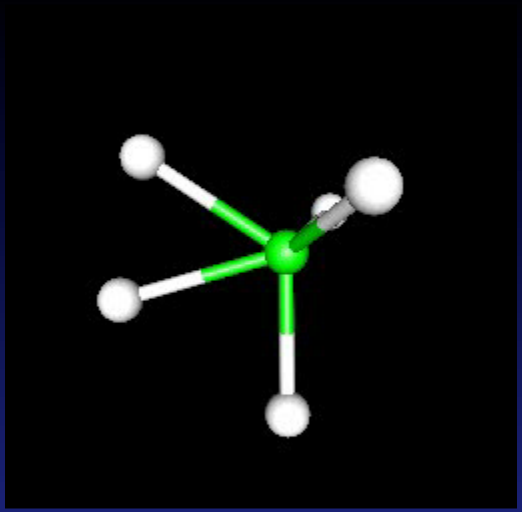
Journal of the American Chemical Society
Volume 127 Issue 13 (April 06, 2005)
CH_5^+: Chemistry's Chameleon Unmasked
Keiran C. Thompson, Deborah L. Crittenden, and Meredith J. T. Jordan
pp 4954 - 4958; **(Article)** DOI: 10.1021/ja0482280



Abstract   Full: HTML / PDF (185K) Supporting Info

Protonated Methane

CH_5^+: A fluxional species



CH_4 + e (hν) → $CH_4^{+\cdot}$ + 2 e (hν')

$CH_4^{+\cdot}$ + CH_4 → CH_5^+ + $CH_3\cdot$

CD_3^+ + H_2 → CD_4H^+ + HD

CD_3^+ + H_2 → $CD_3H_2^+$ + D_2

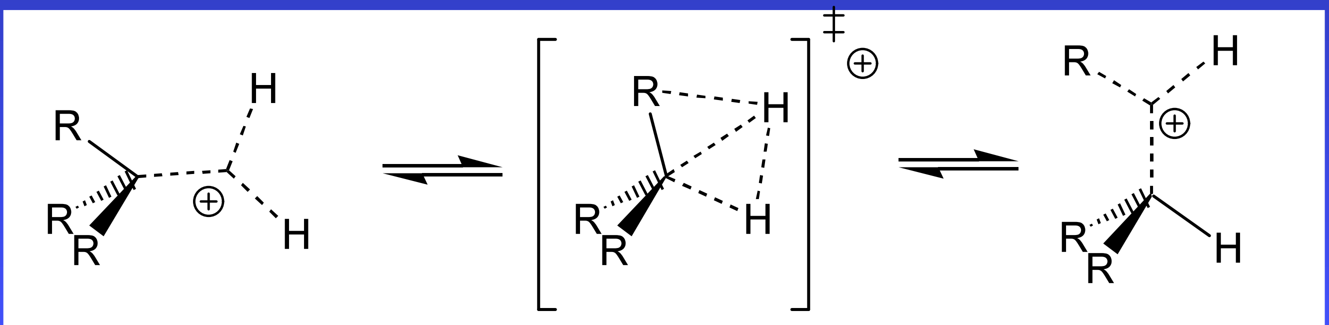
Marx and Parrinello. *Science* **1999.** 284 59 – 6

Oka. Tang and White. *Science* **1999**, 284, 135-137

Asvany *et al. Science* **2005**, 309,1219-1222

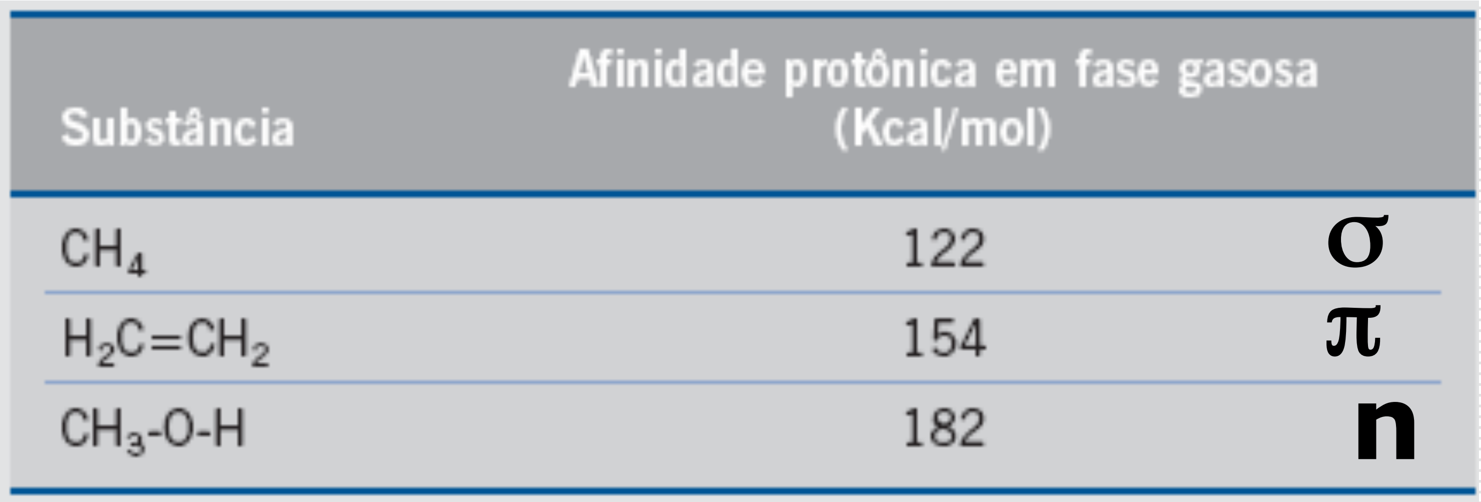
Bowman *et al. Science* **2006**, 311, 5757, 60 - 63

Fluxionality of CH_5^+ and Rearrangements of Carbonium Ions



Ordem de basicidade

$M + H^+ \rightarrow MH^+$ **$AP = -\Delta H_{reação}$**



Substância	Afinidade protônica em fase gasosa (Kcal/mol)	
CH_4	122	σ
$H_2C{=}CH_2$	154	π
CH_3-O-H	182	**n**

$$n > \pi > \sigma$$

Ralph G. Pearson: Dureza e Moleza

Maximum Chemical and Physical Hardness, Ralph G. Pearson, J. Chem. Ed., 76, 267, (1999).

Electronic Properties of Some Inorganic Solids, Ralph G. Pearson, Inorg. Chim. Acta, 270, 252, (1998).

The HSAB Principle - More Quantitative Aspects, Ralph G. Pearson, Inorg. Chim. Acta, 240, 93, (1995).

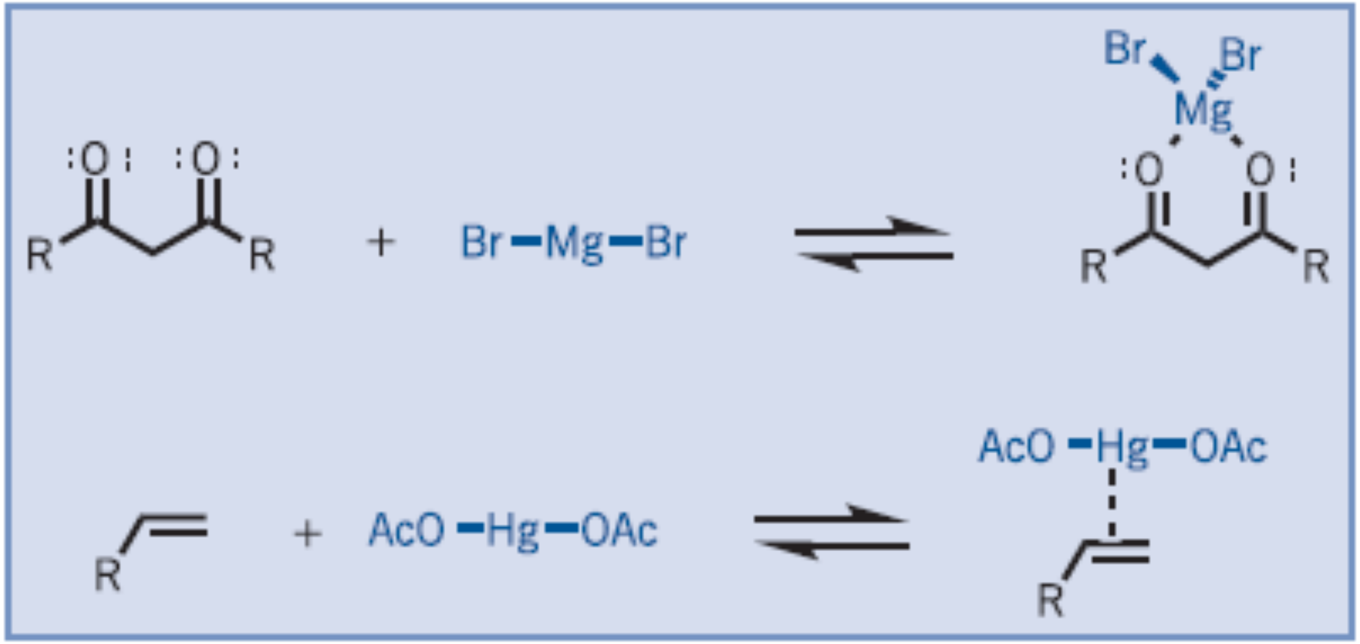
Principle of Maximum Physical Hardness, Ralph G. Pearson, J. Phys. Chem., 98, 1989 (1994).

Bond Energies, Force Constants and Electronegativities, Ralph G. Pearson, J. Mol. Struct. (Thermochem.), 300, 519 (1993).

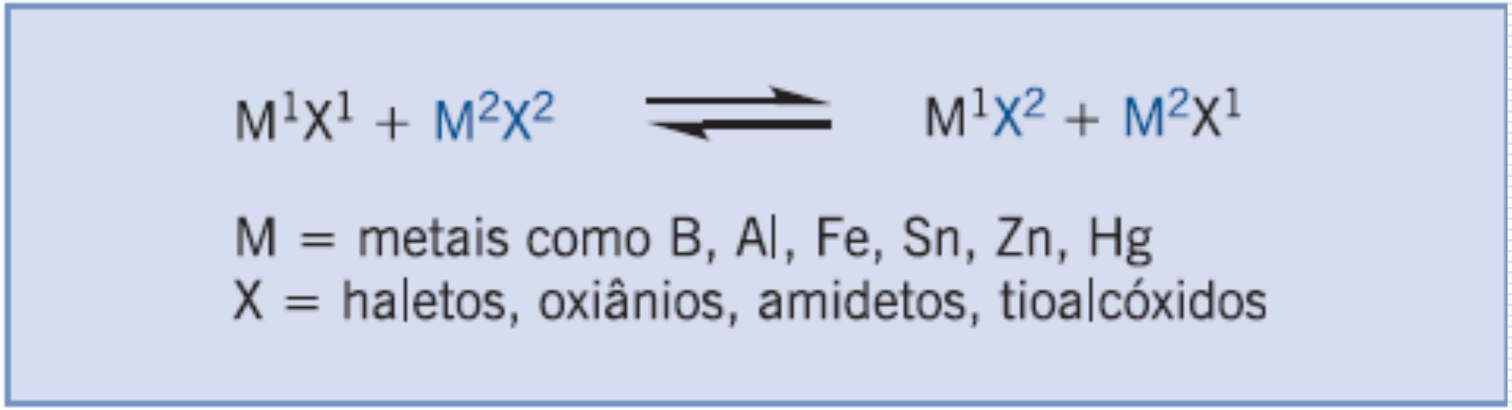
Berzelius 1796:

Porque alguns metais se encontram na natureza sob a forma de sulfetos e outros sob a forma de óxidos, carbonatos, sulfatos ou silicatos?

Porque alguns metais têm afinidade por carbolinas e outros por ligações duplas?



Testou afinidade de íons metálicos por alguns ânions: Posição do equilíbrio

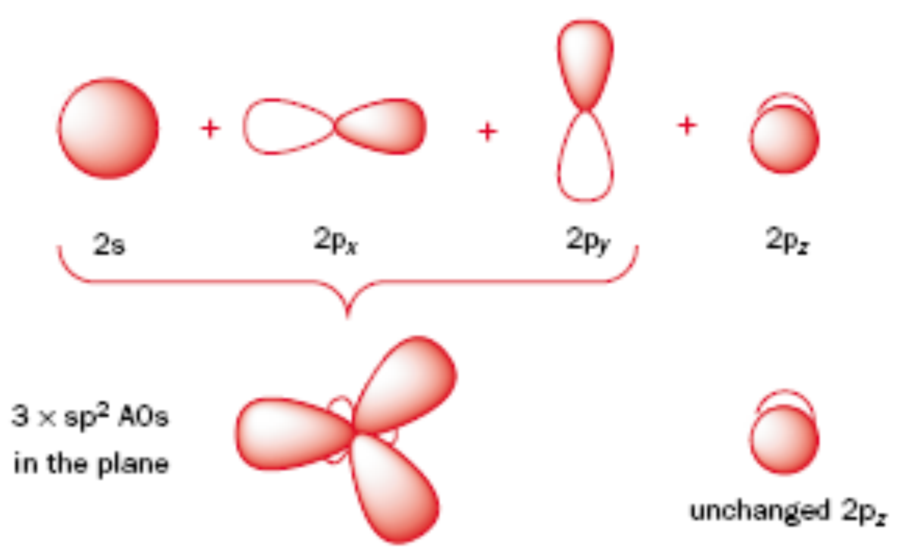


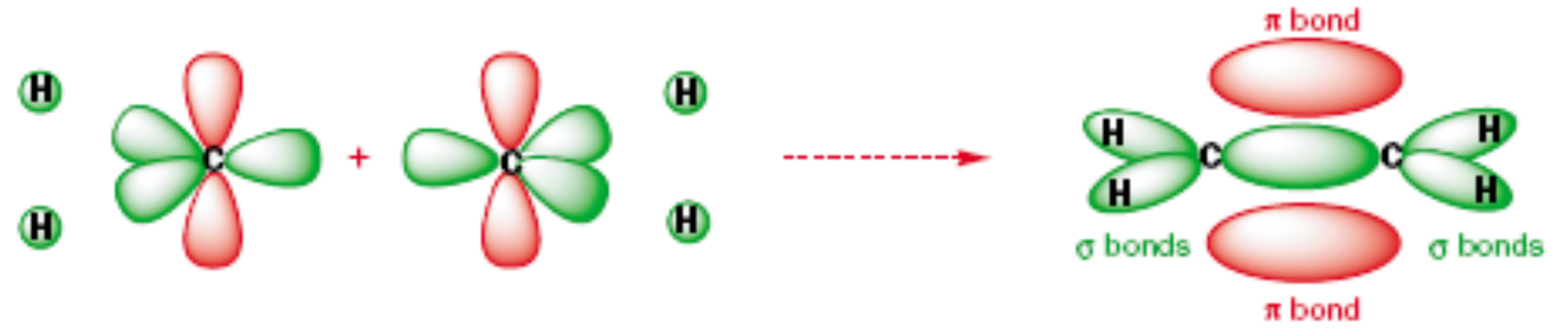
$$M^1X^1 + M^2X^2 \rightleftharpoons M^1X^2 + M^2X^1$$

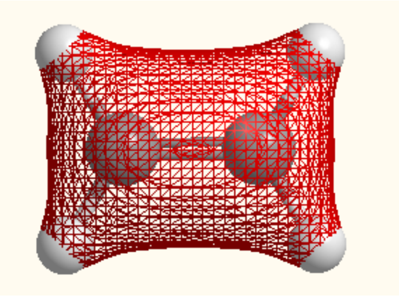
M = metais como B, Al, Fe, Sn, Zn, Hg
X = haletos, oxiânios, amidetos, tioalcóxidos

Orbitais Moleculares

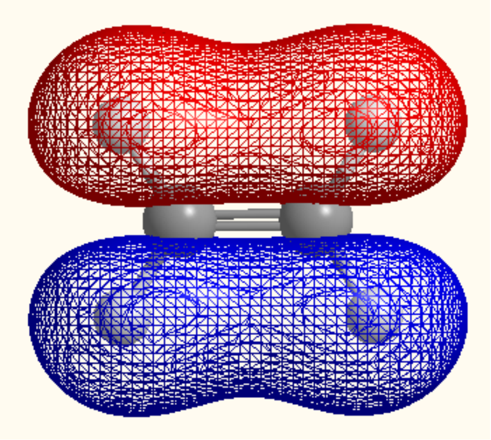
- Uma das formas matemáticas de estudar mundo microscópico
- N orb. Atômicos → N Orb. Mol.
- Ex.: Etileno: 12 OA



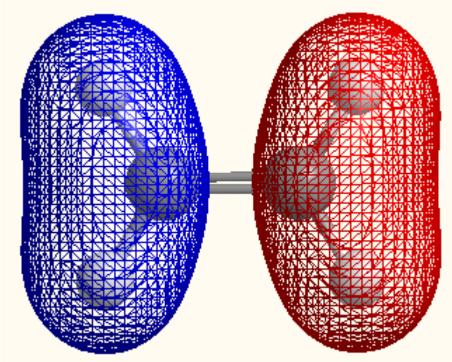




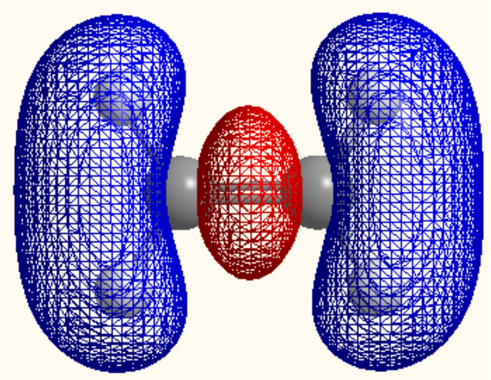
HOMO-5 (N=1)
-33.00 eV



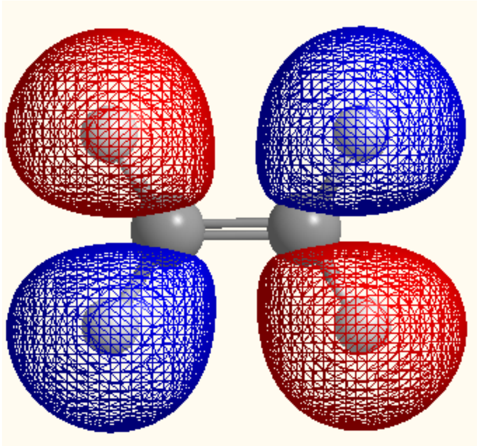
HOMO-4 (N=2)
-21.77 eV



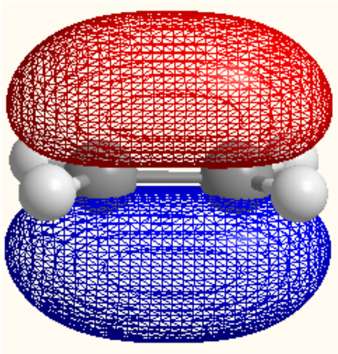
HOMO-3 (N=3)
-15.77 eV



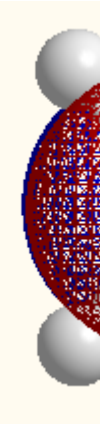
HOMO-2 (N=4)
-14.12 eV

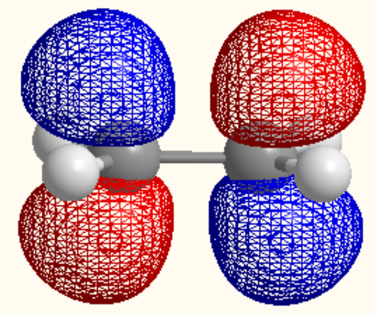


HOMO-1 (N=5)
-11.94 eV

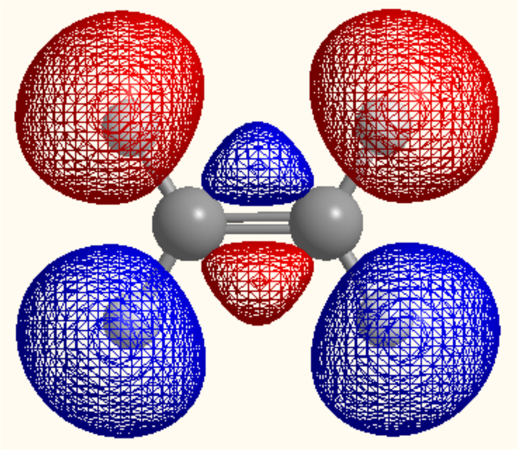


HOMO (N=6)
-10.46 eV

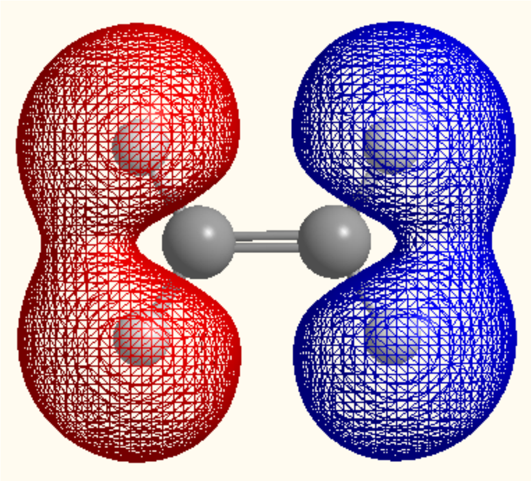




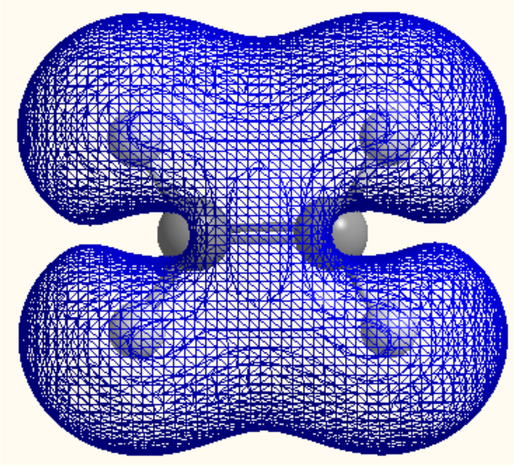
LUMO (N=7)
1.39 eV



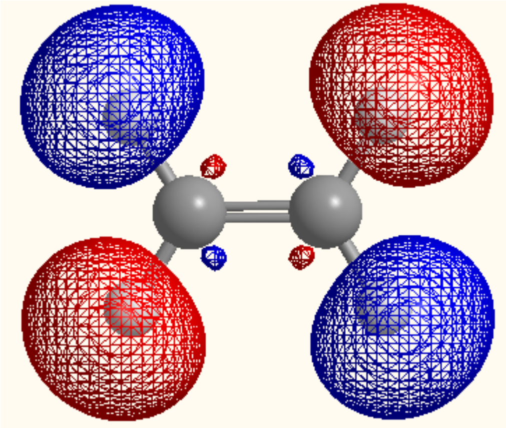
LUMO+1 (N=8)
4.10 eV



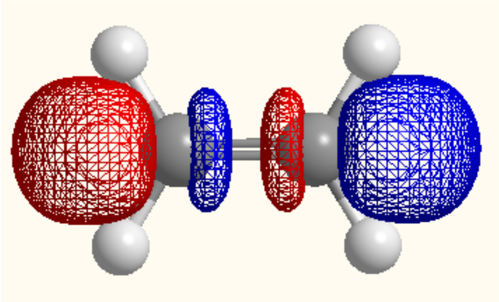
LUMO+2 (N=9)
4.35 eV



LUMO+3 (N=10)
4.98 eV

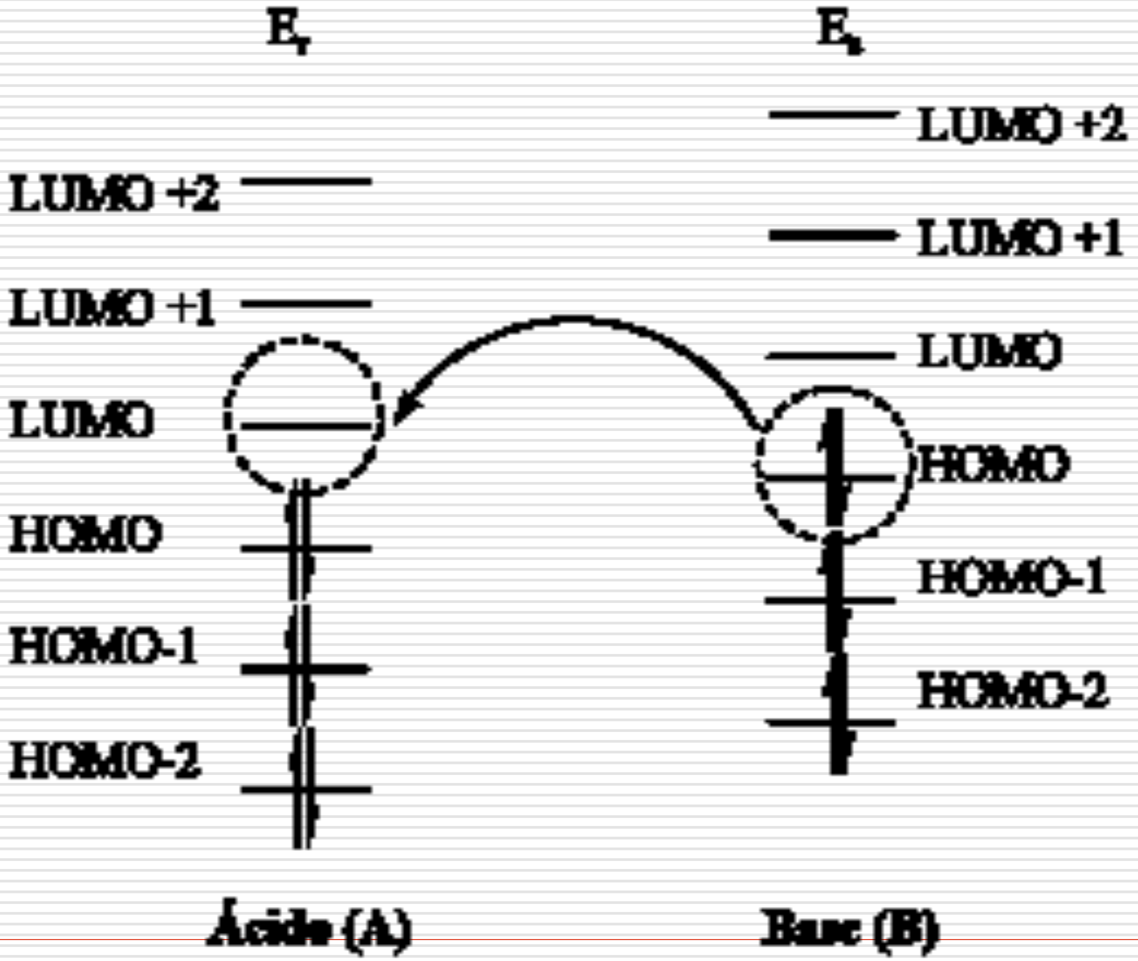


LUMO+4 (N=11)
5.59 eV

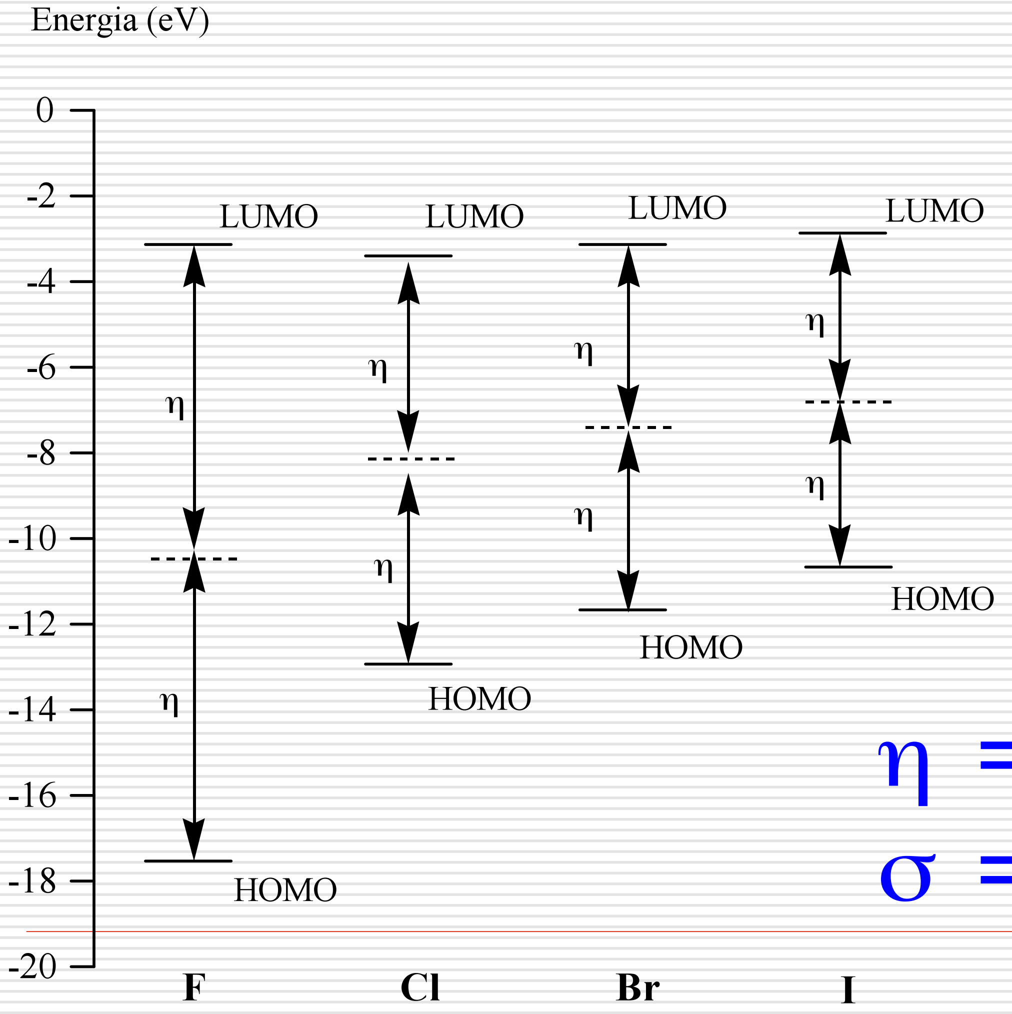


LUMO+5 (N=12)
5.73 eV

Potencial de ionização (PI) = $-E_{HOMO}$ Afinidade eletrônica (AE) = $-E_{LUMO}$



Energia do HOMO e LUMO para os halogênios

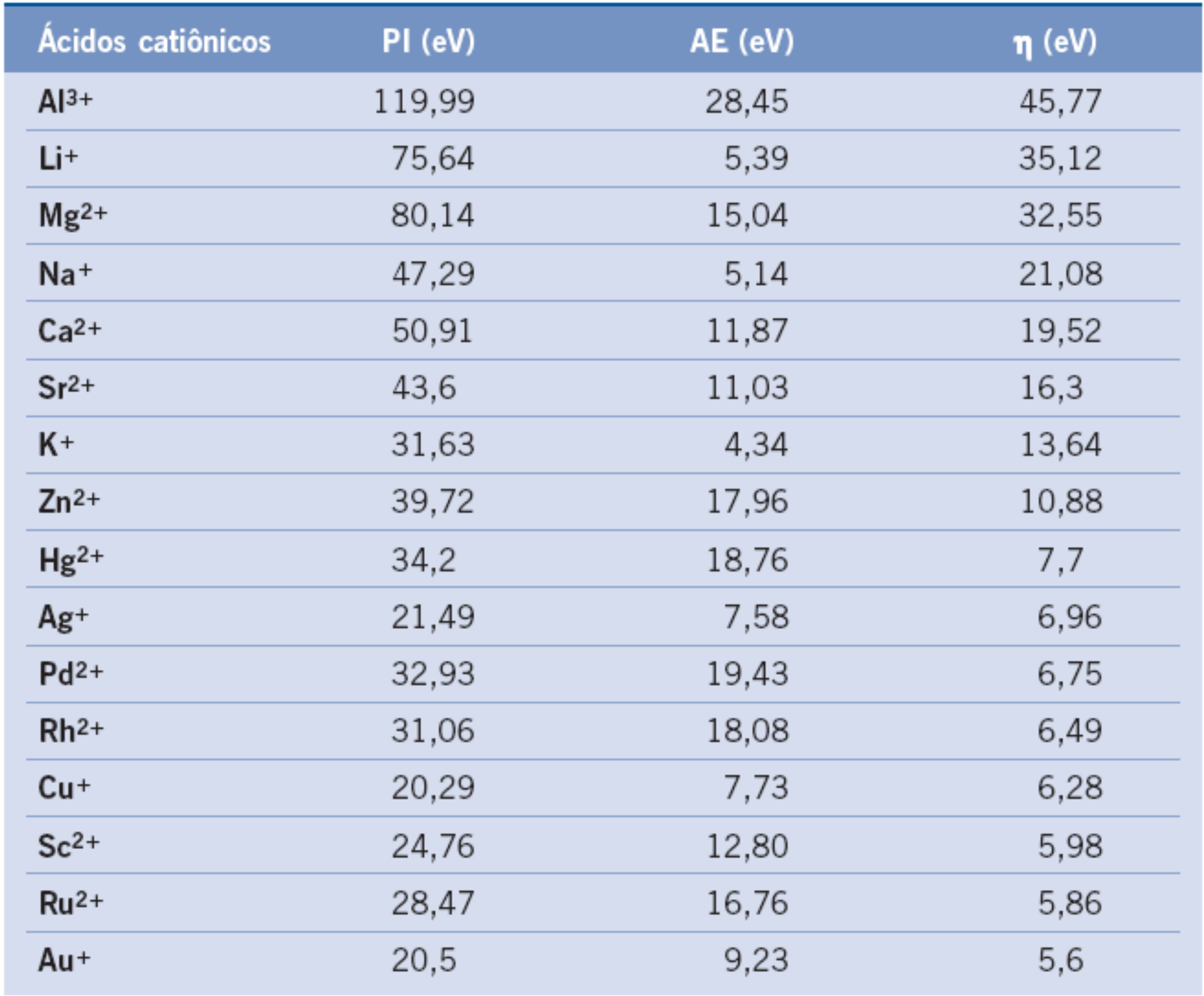


$$\eta = \frac{PI - AE}{2}$$

$$\sigma = 1/\eta$$

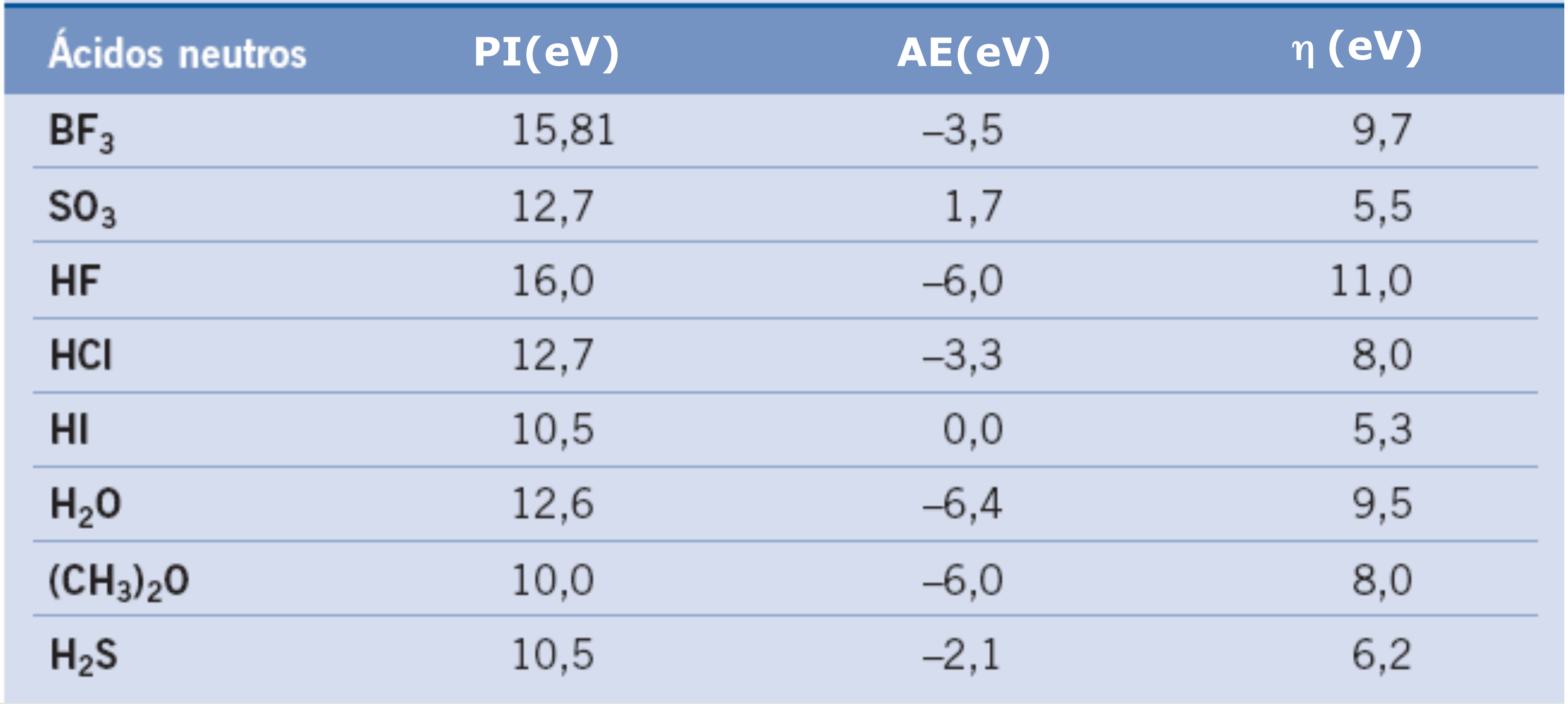
η = dureza global

σ = moleza global



Ácidos catiônicos	PI (eV)	AE (eV)	η (eV)
Al^{3+}	119,99	28,45	45,77
Li^{+}	75,64	5,39	35,12
Mg^{2+}	80,14	15,04	32,55
Na^{+}	47,29	5,14	21,08
Ca^{2+}	50,91	11,87	19,52
Sr^{2+}	43,6	11,03	16,3
K^{+}	31,63	4,34	13,64
Zn^{2+}	39,72	17,96	10,88
Hg^{2+}	34,2	18,76	7,7
Ag^{+}	21,49	7,58	6,96
Pd^{2+}	32,93	19,43	6,75
Rh^{2+}	31,06	18,08	6,49
Cu^{+}	20,29	7,73	6,28
Sc^{2+}	24,76	12,80	5,98
Ru^{2+}	28,47	16,76	5,86
Au^{+}	20,5	9,23	5,6

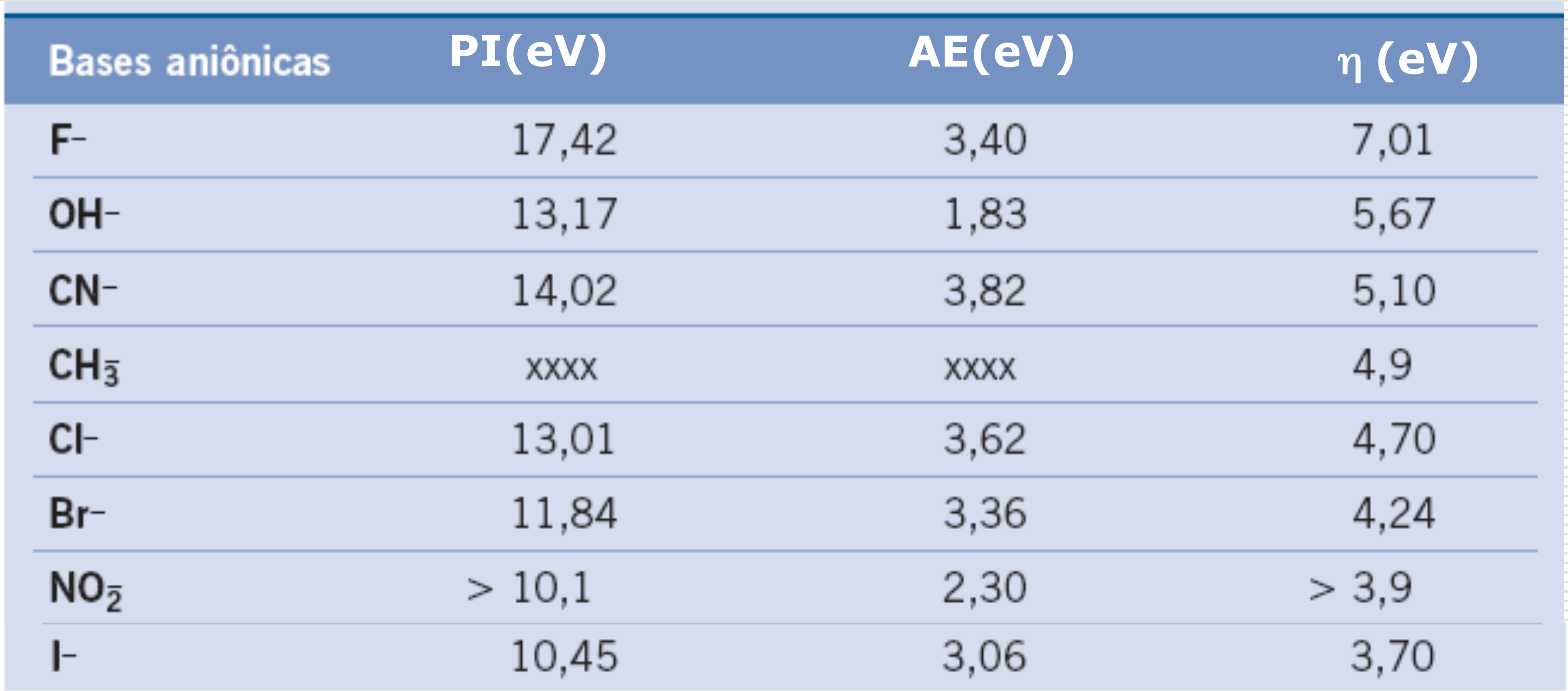
- ☐ PI varia mais que AE



Ácidos neutros	PI(eV)	AE(eV)	η (eV)
BF_3	15,81	–3,5	9,7
SO_3	12,7	1,7	5,5
HF	16,0	–6,0	11,0
HCl	12,7	–3,3	8,0
HI	10,5	0,0	5,3
H_2O	12,6	–6,4	9,5
$(CH_3)_2O$	10,0	–6,0	8,0
H_2S	10,5	–2,1	6,2

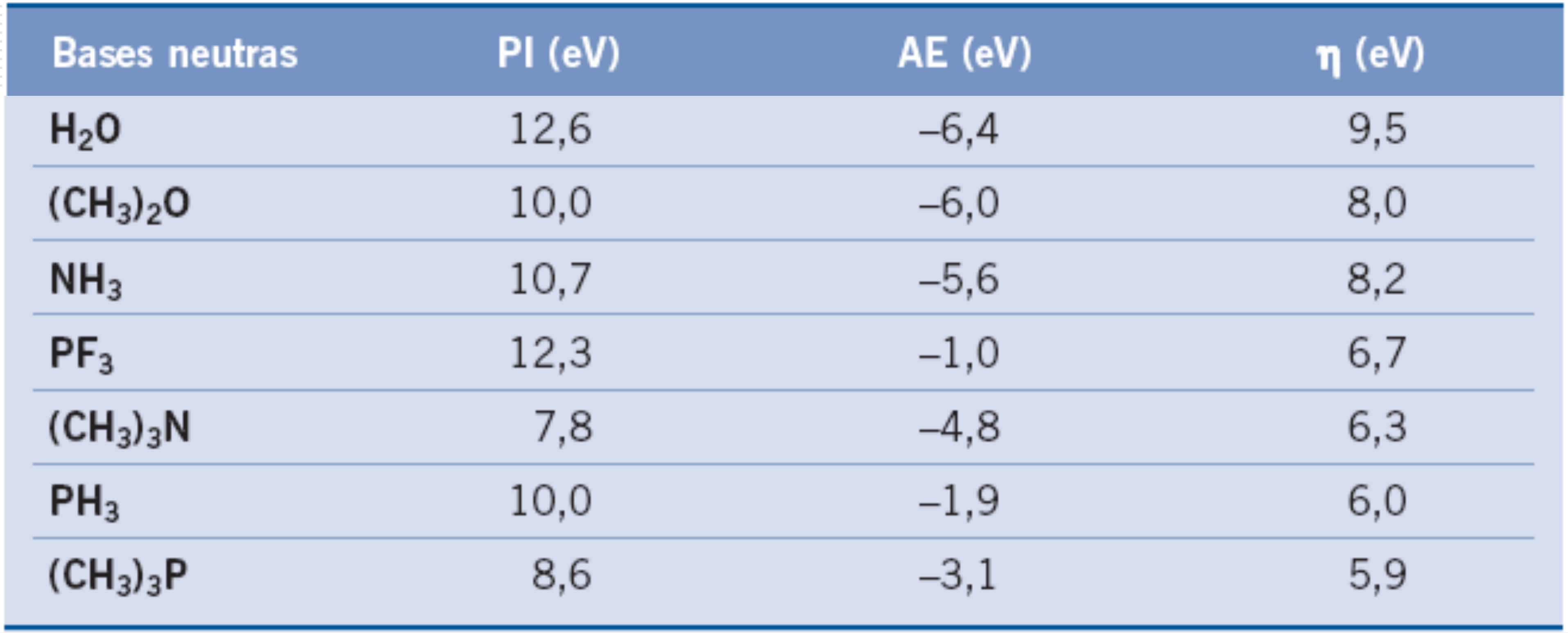
HF x HCl x HI

H_2O x H_2S x $(CH_3)_2O$



Bases aniônicas	PI(eV)	AE(eV)	η (eV)
F^-	17,42	3,40	7,01
OH^-	13,17	1,83	5,67
CN^-	14,02	3,82	5,10
CH_3^-	xxxx	xxxx	4,9
Cl^-	13,01	3,62	4,70
Br^-	11,84	3,36	4,24
NO_2^-	> 10,1	2,30	> 3,9
I^-	10,45	3,06	3,70

F^- x Cl^- x Br^-x I^-



Bases neutras	PI (eV)	AE (eV)	η (eV)
H_2O	12,6	–6,4	9,5
$(CH_3)_2O$	10,0	–6,0	8,0
NH_3	10,7	–5,6	8,2
PF_3	12,3	–1,0	6,7
$(CH_3)_3N$	7,8	–4,8	6,3
PH_3	10,0	–1,9	6,0
$(CH_3)_3P$	8,6	–3,1	5,9

H_2O x $(CH_3)_2O$

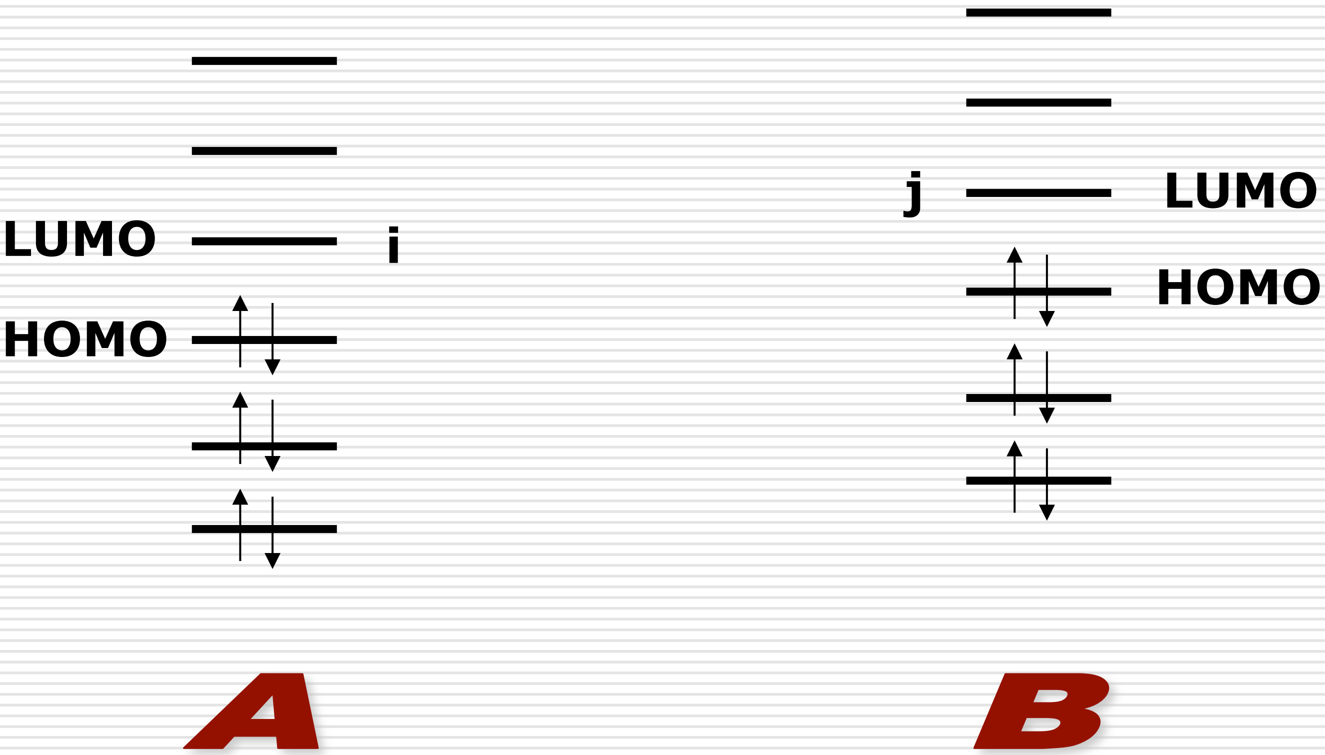
NH_3 x PH_3 x $(CH_3)_3N$ x $(CH_3)_3P$

Ácidos e Bases

- **Pearson**: Ácidos/Bases Duros e Moles (1963)

Boa interação:	Ácido Duro - Base Dura Ácido Mole – Base Mole
Má interação:	Ácido Mole - Base Dura Ácido Duro – Base Mole

Interação entre Reagentes: MOs



HOMO: ***Highest Occupied Molecular Orbital***
LUMO: Lowest Unoccupied Molecular Orbital

Energia de Interação entre Reagentes

$$\textbf{Energia Interação entre A e B} = \underbrace{\overbrace{\left(\textbf{Interação Carga-Carga}\right)}^{\textit{Longa Distância}}}_{\textit{Dureza}} + \underbrace{\overbrace{\underbrace{\left(\textbf{Interação Ocup. A com Ocup. B}\right)}_{\textit{Repulsivo}\sim\textit{cte}} + \underbrace{\left(\textbf{Interação Desocup. A com Desocup. B}\right)}_{= \textit{0}} + \underbrace{\left(\textbf{Interação Ocupados com Desocupados}\right)}_{\textit{Atrativo}}}^{\textit{Curta Distância}}}_{\textit{Moleza}}$$

Energia de Interação entre Reagentes

$$\textbf{Energia Interação entre A e B} = \overbrace{\underbrace{\left(\frac{1}{4\pi\varepsilon_o}\sum_{k<l}\frac{q_k q_l}{r_{kl}}\right)}_{\textbf{\textit{Lei Coulomb}}}}^{\textbf{\textit{Longa Distância}}} + \overbrace{\left(\textbf{Repulsivo Cte}\right) + \mathbf{0} + \underbrace{\left(\sum\sum\frac{Outros}{E_r - E_s}\right)}_{\textbf{\textit{Atrativo}}}}^{\textbf{\textit{Curta Distância}}}$$

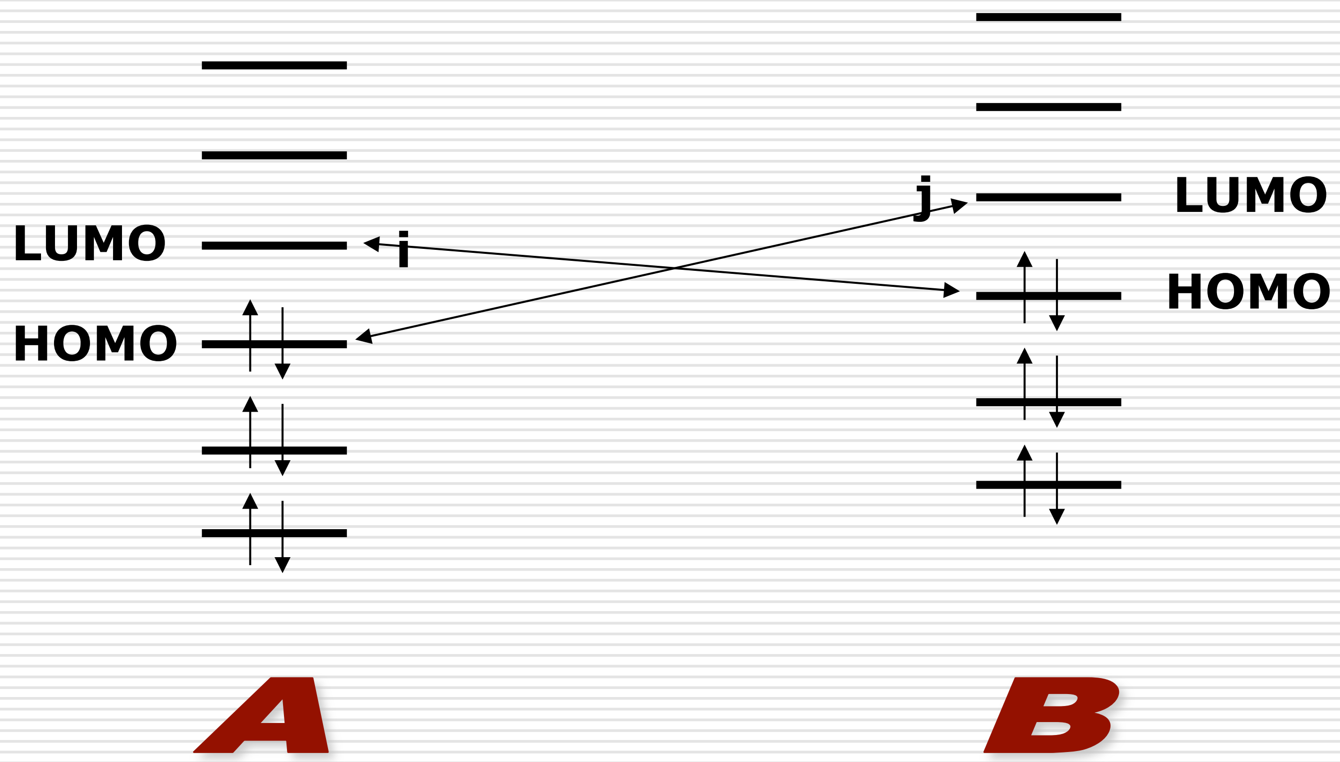
Quanto menor a diferença energia entre orbitais ocupados e desocupados, maior a energia de interação

Equação de Klopman e Salem

$$E_{\text{interação}} = -\sum_{ab}(q_a + q_b)\beta_{ab}S_{ab} \quad + \sum_{k<l}\frac{q_k q_l}{\varepsilon r_{kl}} \quad + \sum_{r}^{ocup}\sum_{s}^{não-ocup} - \sum_{r}^{ocup}\sum_{s}^{não-ocup}\frac{2(\sum_{ab} c_{ra}c_{sb}\beta_{ab})^2}{E_r - E_s}$$

$$Ocupado-Ocupado \qquad Eletrostático \qquad Sobreposição\ Orbitalar$$

Interação entre Reagentes: MOs



HOMO: ***Highest Occupied Molecular Orbital***
LUMO: Lowest Unoccupied Molecular Orbital

Orbitais de Fronteira: HOMO e LUMO

- Orbitais de menor diferença de energia são o par HOMO de mais alta energia com o LUMO de mais baixa energia entre as duas espécies

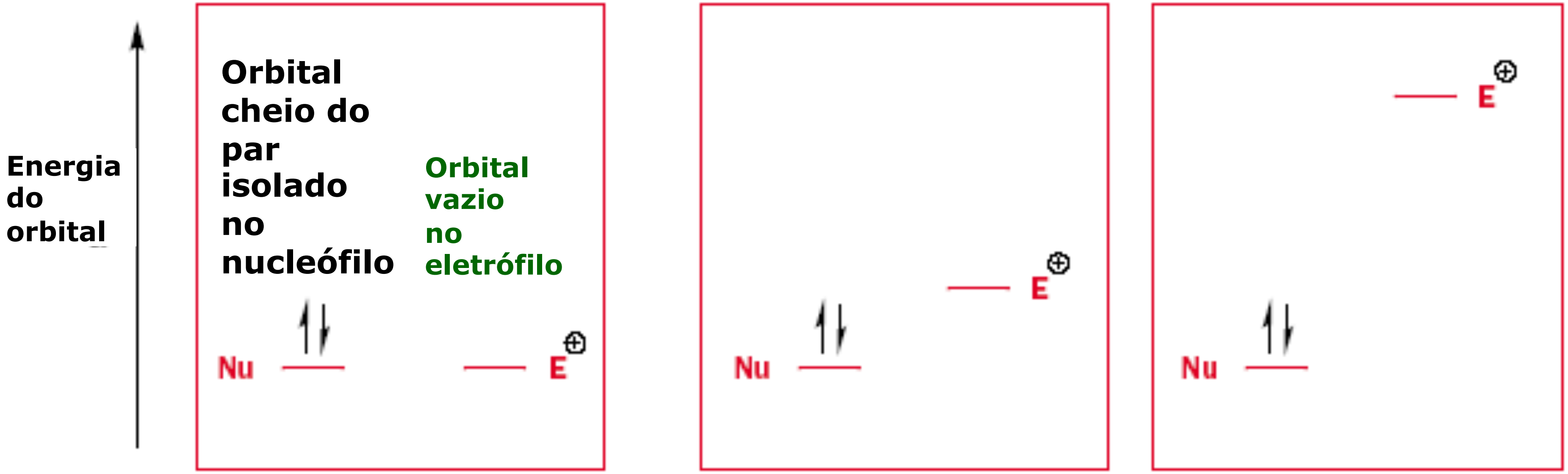
HOMO mais alto

Base/Nucleófilo

LUMO mais baixo

Ácido/Eletrófilo

Orbitais de Fronteira: HOMO e LUMO



Orbitais têm mesma energia

Pequena diferença de energia entre os orbitais cheio e vazio

Grande diferença de energia entre os orbitais cheio e vazio

Transferência de 1 elétron
Complexos de transferência de carga

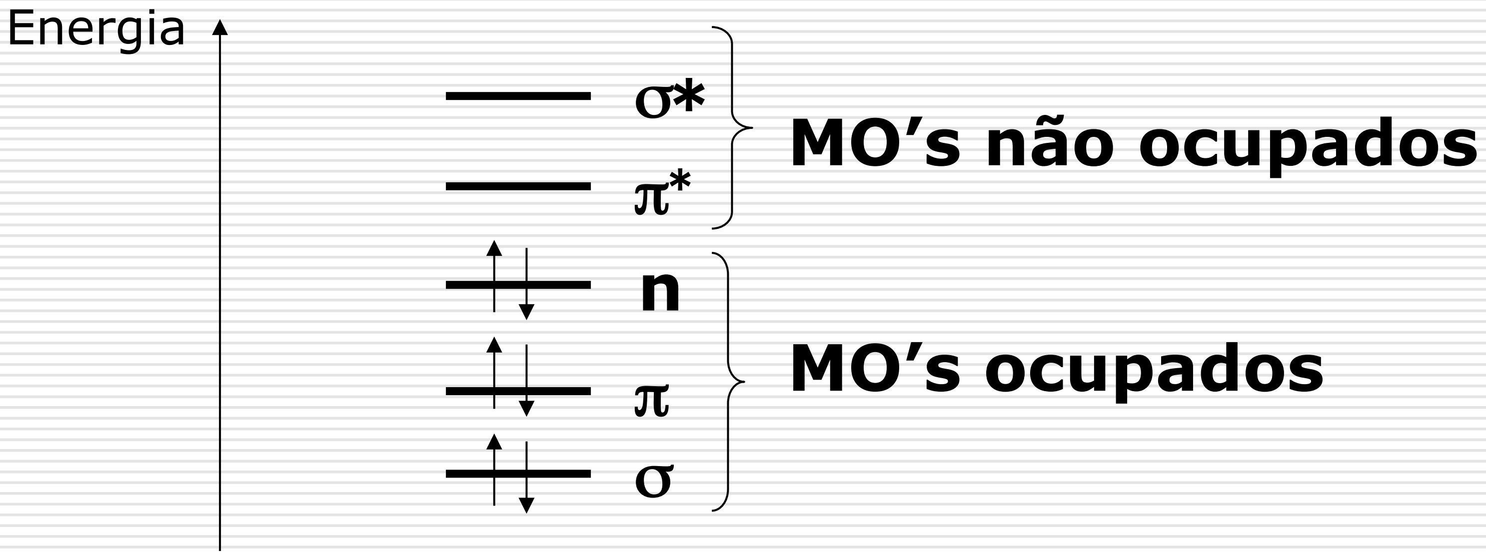
Interação mole-mole não desprezível

Interação duro-duro domina

Bases (nucleófilos)	Ácidos (eletrófilos)
Duros H_2O, ^-OH, F^- $MeCO_2$, PO_4^{-3}, SO_4^{-2}, Cl^-, CO_3^{-2}, ClO_4^-, NO_3^- ROH, RO^-, R_2O NH_3, RNH_2, N_2O_4	**Duros** H^+, Li^+, Na^+, K^+ Be^{2+}, Mg^{2+}, Ca^{2+} Al^{3+}, Ga^{3+} Cr^{3+}, Co^{3+}, Fe^{3+} CH_3Sn^{3+} Si^{4+}, Ti^{4+} Ce^{3+}, Ti^{4+} $(CH_3)_2Sn^{2+}$ $BeMe_2$, BF_3, $B(RO)_3$ $AlMe_3$, $AlCl_3$, AlH_3 RPO^{2+}, $ROPO^{2+}$ RSO_2^+, $ROSO_2^+$, SO_3 I^{7+}, I^{5+}, Cl^{7+}, Cr^{6+} RCO^+, CO_2, NC^+ HX (moléculas com capacidade de fazer ligações de hidrogênio)
De fronteira $PhNH_2$, C_5H_5N, N_3^-, Br^- NO_2^-, SO_3^{2-}	**De fronteira** Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, BMe_3, SO_2, NO^+, R_3C^+, $C_6H_5^+$

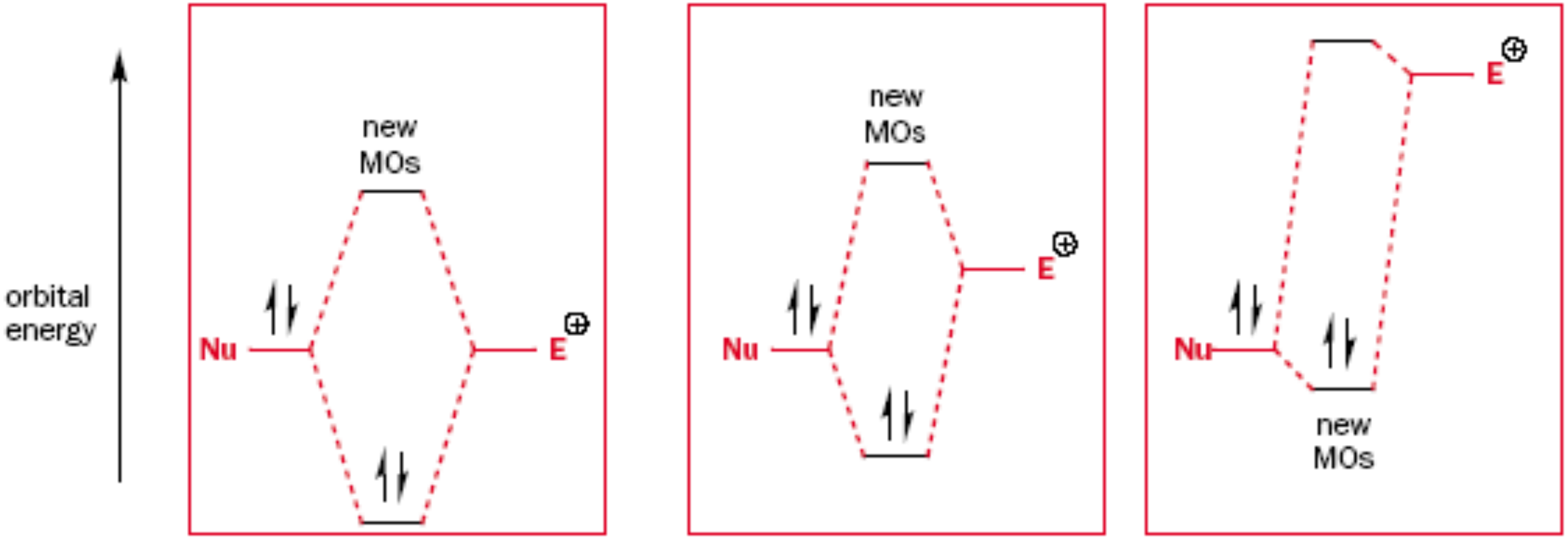
Moles	**Moles**
R_2S, RSH, –SH	Cu^+, Ag^+, Au, Tl, Hg
–I, –SCN, $S_2O_3^{-2}$	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, $MeHg^+$, $CO(CN)_5^{2-}$
R_3P, R_3As, $(RO)_3P$	Tl^{3+}, $Tl(CH_3)_3$, BH_3
–CN, RCN, CO	RS^+, RSe^+, RTe^+
C_2H_4, C_6H_6	I^+, Br^+, HO^+, RO^+
–H, –R	I_2, Br_2, ICN
	Trinitrobenzeno
	Cloranil, quinonas
	$(NC)_2=C(CN)_2$, etc.
	O, Cl, Br, I, N, RO·, RO_2·
	M° (metais)
	CH_2, carbenos

HOMO: O Guardião do par de elétrons



- Força da base

$$\mathbf{n} > \pi > \sigma$$



orbitals have the same energy

small difference in energy of filled and empty orbitals

large difference in energy of filled and empty orbitals

A escala de acidez de Hammett (H_o): Acidez "efetiva" além do intervalo convencional de pH

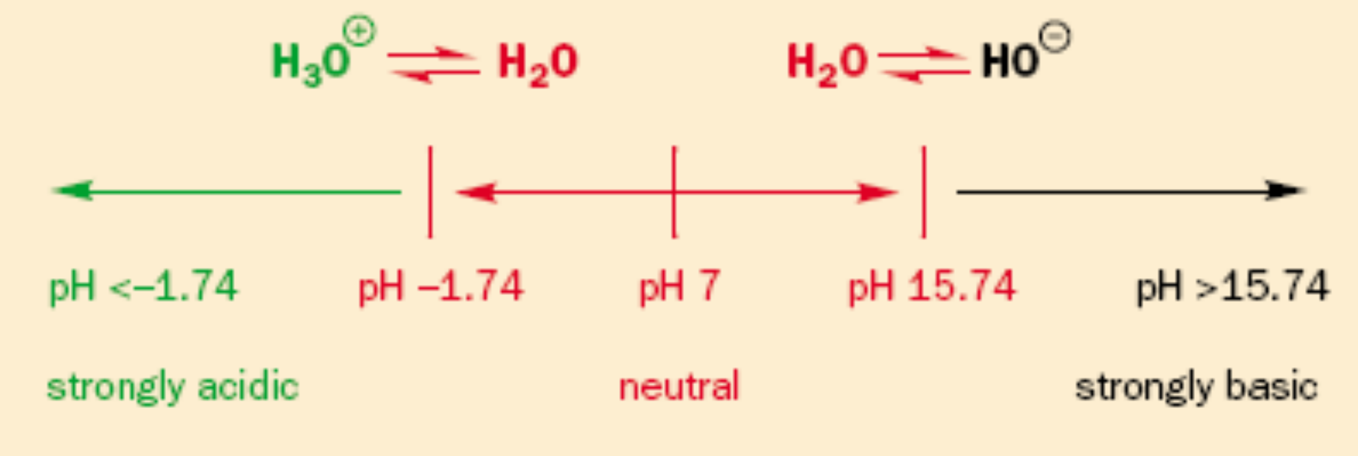
Louis Plack Hammett (1894-1987)

$$BH^+ \rightleftharpoons H^+ + B$$

Escala de pH: ácido mais forte em H_2O é o H_3O^+ e a base mais forte é o OH^-

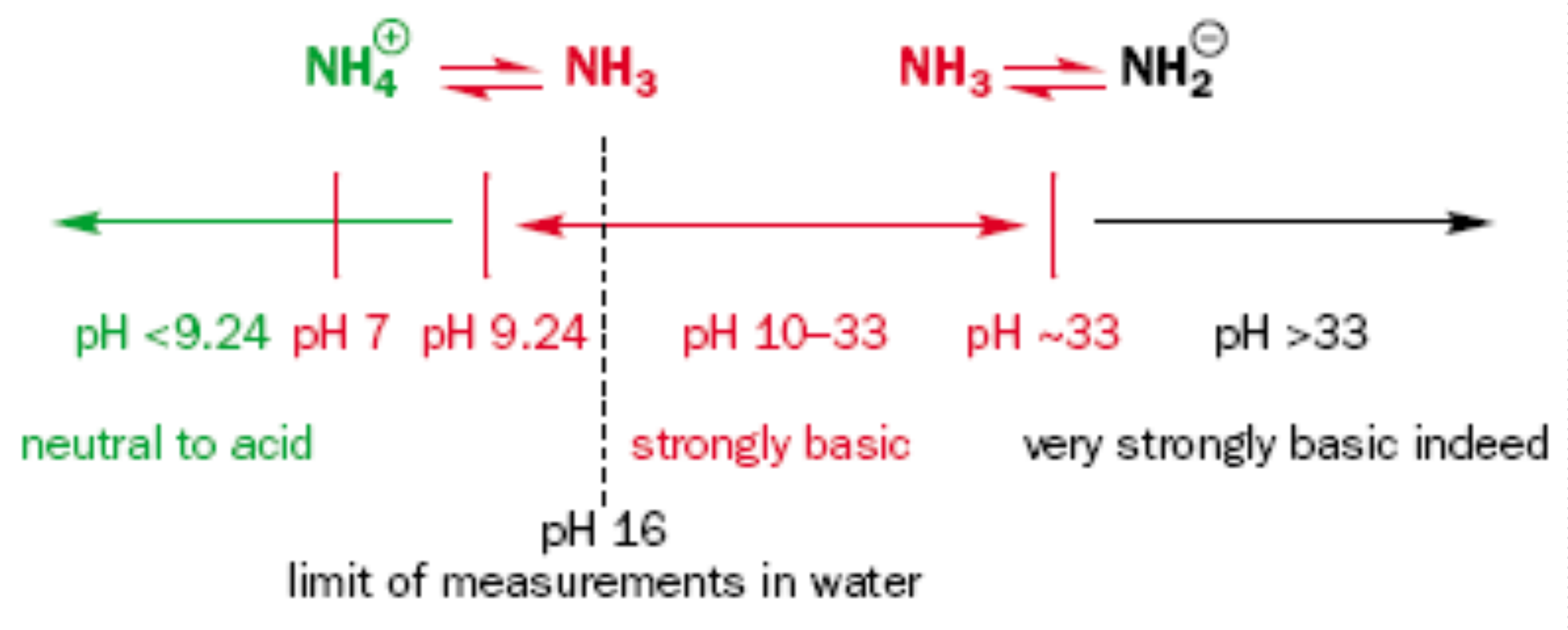
$pK_a(H_2O) = 15.74$

$pK_a(H_3O^+) = -1.74$



- **Adição de base mais forte que OH^- somente dá mais OH^- pela desprotonação da água**
- **Adição de ácido mais forte que H_3O^+ somente dá mais H_3O^+ pela protonação da água**

Em amônia


$NH_4^{\oplus} \rightleftharpoons NH_3$
$NH_3 \rightleftharpoons NH_2^{\ominus}$
pH <9.24
pH 7
pH 9.24
pH 10–33
pH ~33
pH >33
neutral to acid
strongly basic
very strongly basic indeed
pH 16
limit of measurements in water

$$BH^+ \rightleftharpoons H^+ + B$$

Equação de Henderson-Hasselbalch

$$pK_a = pH + \log \frac{[HB^+]}{[B]}$$

Equação de Hammett

$$pK_a = H_0 + \log \frac{[HB^+]}{[B]}$$

atividade de X

$$a_X = [X] \cdot \gamma X$$

coeficiente de atividade de X

concentração de X

$$H_0 = -\log \left(a_{H^+} \cdot \frac{\gamma B}{\gamma BH^+} \right)$$

Função acidez de Hammett H_o

- H_o de Hammett pode ser pensada como o “pH efetivo” de uma solução não aquosa
- Escala se refere a uma solução hipotética formada se tivesse a mesma relação de equilíbrio ácido/base conjugada encontrada na solução aquosa

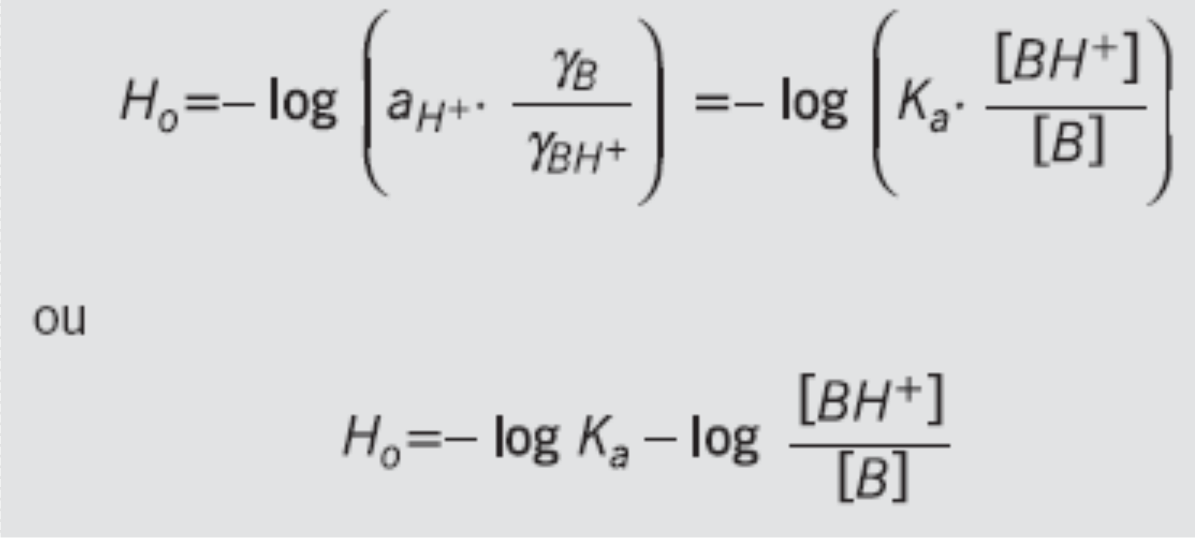
$BH^+ \rightarrow B + H^+$

$$K_a = (K_a)_{BH^+} = \frac{a_{H^+} \cdot a_B}{a_{BH^+}}$$

$$K_a = \frac{a_{H^+} \cdot [B] \cdot \gamma_B}{[BH^+] \cdot \gamma_{BH^+}} = K_a \frac{[BH^+]}{[B]} = a_{H^+} \cdot \frac{\gamma_B}{\gamma_{BH^+}}$$

$$H_o = -\log \underbrace{\left(a_{H^+} \cdot \frac{\gamma_B}{\gamma_{BH^+}} \right)}$$

Capacidade de protonação do meio
+ comportamento não ideal

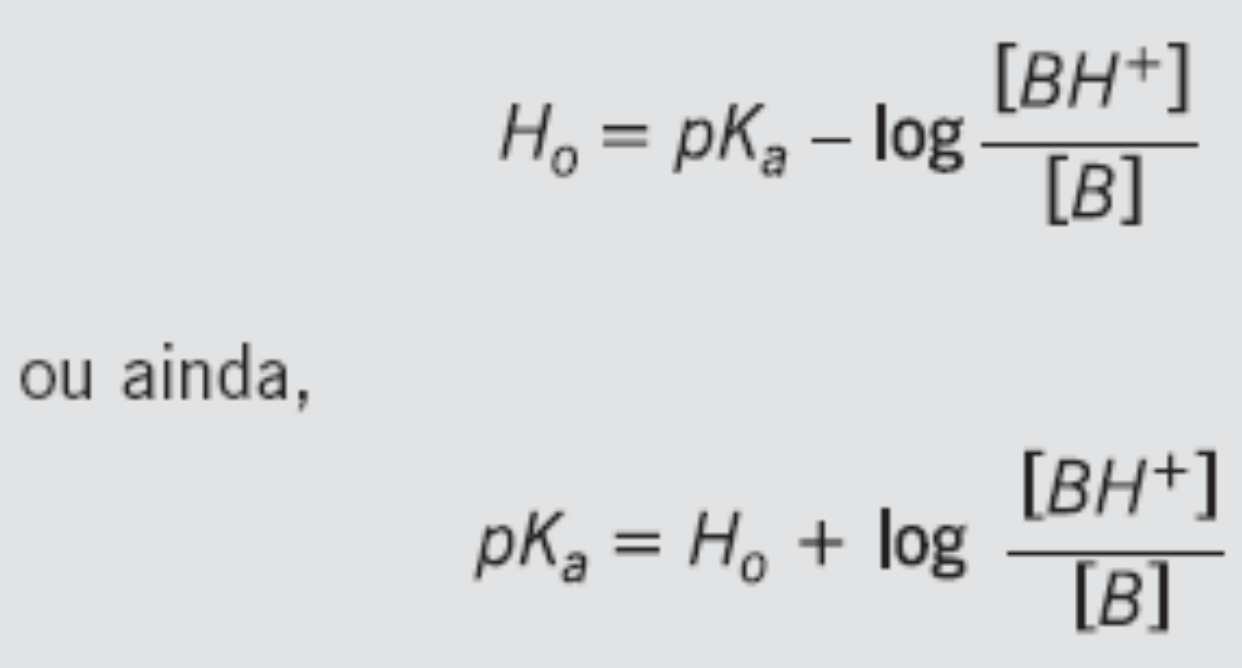


$$H_o = -\log\left(a_{H^+}\cdot\frac{\gamma_B}{\gamma_{BH^+}}\right) = -\log\left(K_a\cdot\frac{[BH^+]}{[B]}\right)$$

ou

$$H_o = -\log K_a - \log\frac{[BH^+]}{[B]}$$

Como $pK_a = -\log K_a$

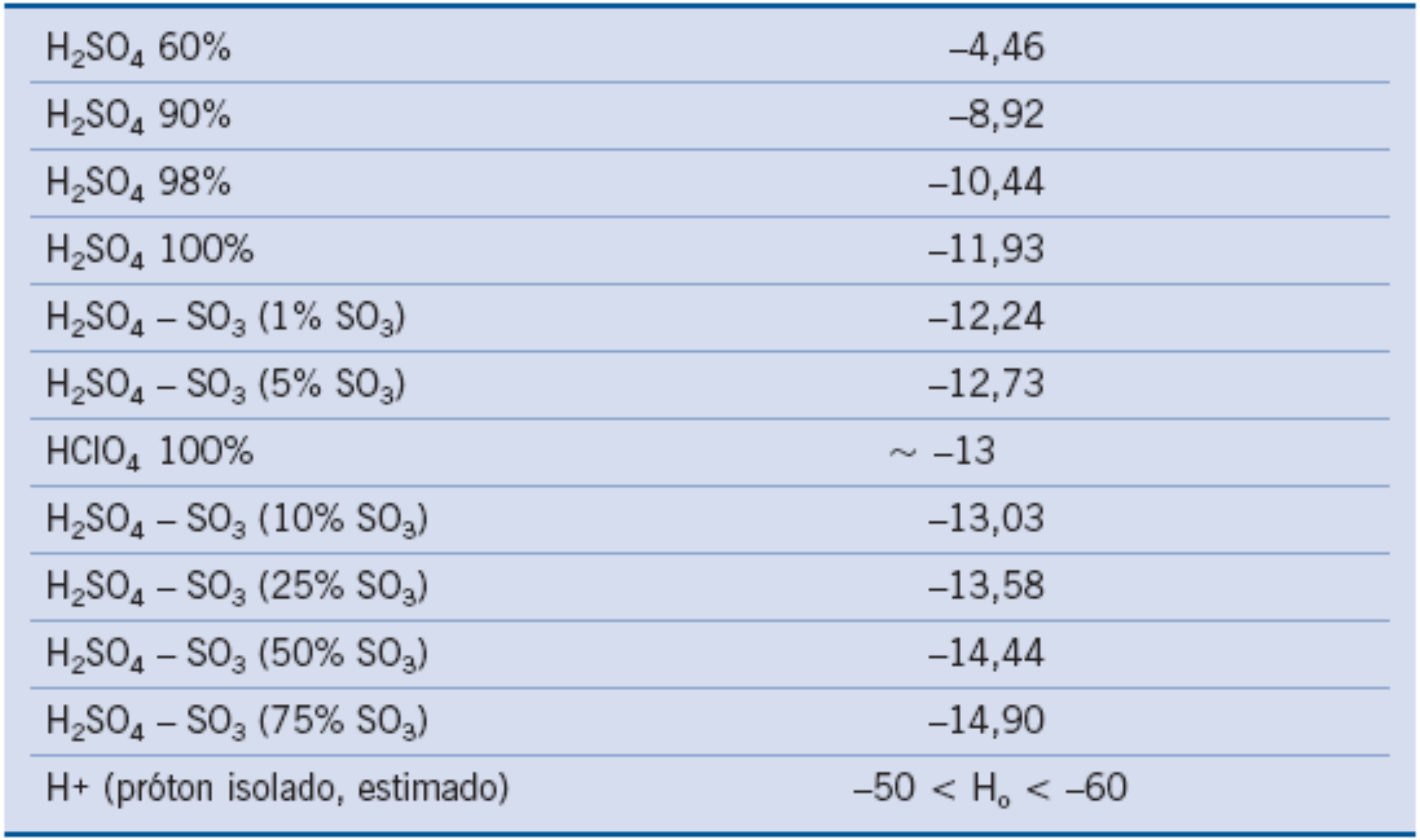


$$H_o = pK_a - \log\frac{[BH^+]}{[B]}$$

ou ainda,

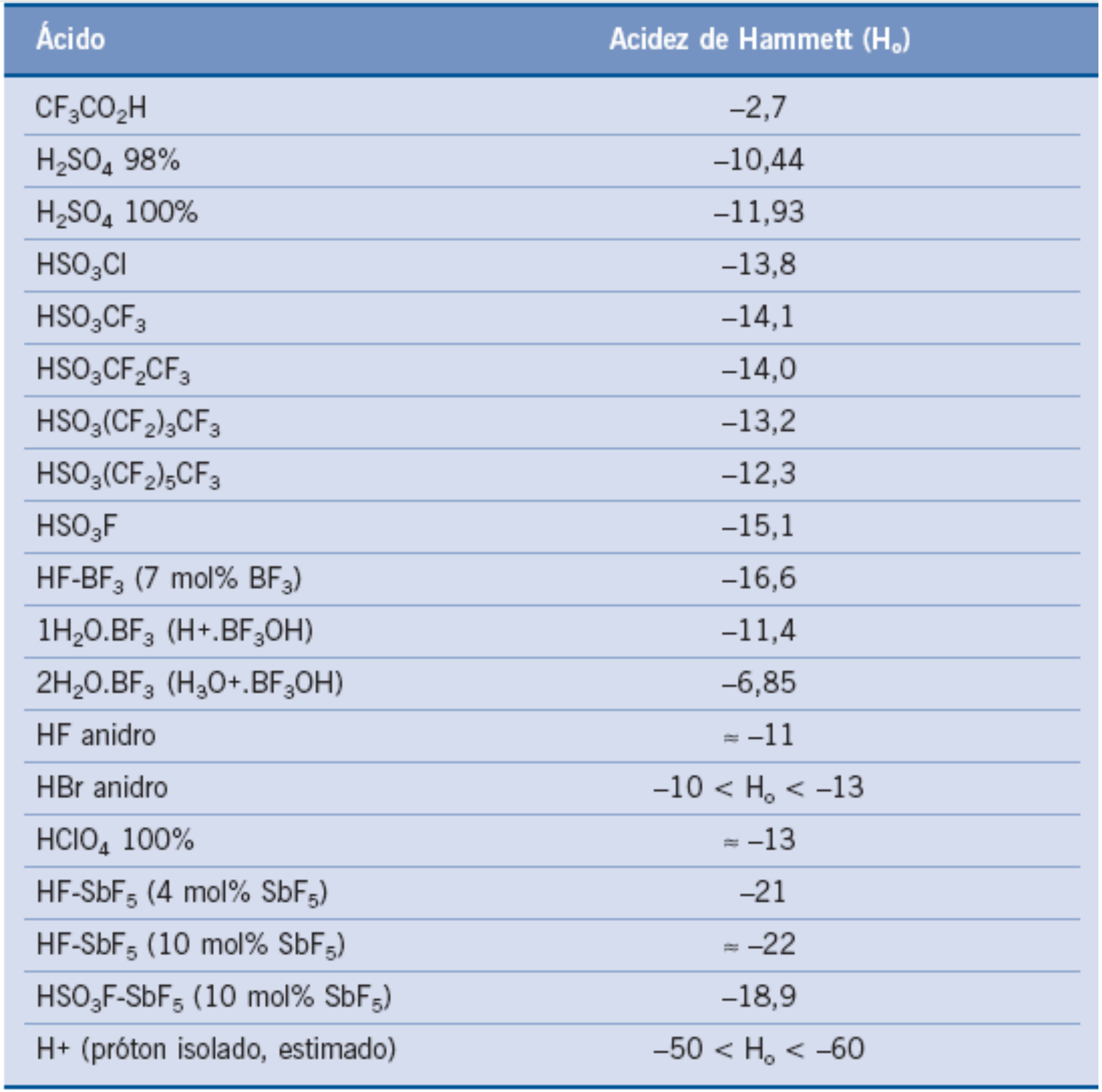
$$pK_a = H_o + \log\frac{[BH^+]}{[B]}$$

Acidez (H_o) de Misturas de H_2SO_4/ H_2O/SO_3



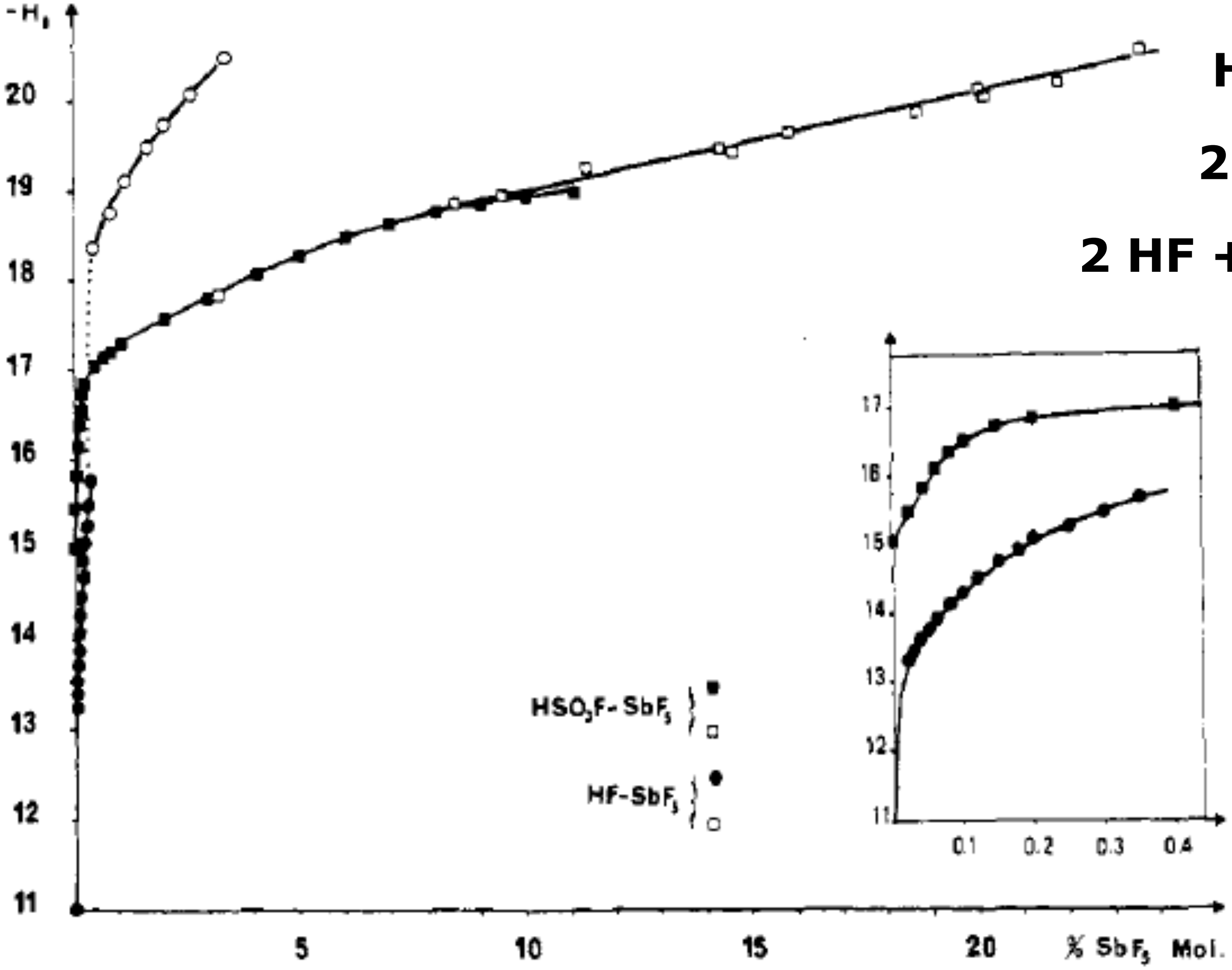
H_2SO_4 60%	–4,46
H_2SO_4 90%	–8,92
H_2SO_4 98%	–10,44
H_2SO_4 100%	–11,93
H_2SO_4 – SO_3 (1% SO_3)	–12,24
H_2SO_4 – SO_3 (5% SO_3)	–12,73
$HClO_4$ 100%	~ –13
H_2SO_4 – SO_3 (10% SO_3)	–13,03
H_2SO_4 – SO_3 (25% SO_3)	–13,58
H_2SO_4 – SO_3 (50% SO_3)	–14,44
H_2SO_4 – SO_3 (75% SO_3)	–14,90
H+ (próton isolado, estimado)	$-50 < H_o < -60$

Função Acidez de Hammett (H_o) para alguns sistemas ácidos



Ácido	Acidez de Hammett (H_o)
CF_3CO_2H	–2,7
H_2SO_4 98%	–10,44
H_2SO_4 100%	–11,93
HSO_3Cl	–13,8
HSO_3CF_3	–14,1
$HSO_3CF_2CF_3$	–14,0
$HSO_3(CF_2)_3CF_3$	–13,2
$HSO_3(CF_2)_5CF_3$	–12,3
HSO_3F	–15,1
HF-BF_3 (7 mol% BF_3)	–16,6
$1H_2O.BF_3$ ($H^+.BF_3OH$)	–11,4
$2H_2O.BF_3$ ($H_3O^+.BF_3OH$)	–6,85
HF anidro	≈ –11
HBr anidro	$-10 < H_o < -13$
$HClO_4$ 100%	≈ –13
HF-SbF_5 (4 mol% SbF_5)	–21
HF-SbF_5 (10 mol% SbF_5)	≈ –22
HSO_3F-SbF_5 (10 mol% SbF_5)	–18,9
H^+ (próton isolado, estimado)	$-50 < H_o < -60$

Variando H_o: Mistura de ácidos de Bronsted e de Lewis



$HA + HB \rightarrow H_2A^+ + B^-$

$2\ HA + L \rightarrow H_2A^+ + AL^-$

$2\ HF + SbF_5 \rightarrow H_2F^+ + SbF_6^-$

Sommer, Schwartz, Rimmelin, Canivet JACS **1978**, *100*, 2576

Meios fortemente básicos

Uma função análoga para meios fortemente básicos pode ser obtida através de um raciocínio semelhante.

$$H_- = pK_a - \log [B^-] / [HB]$$

Alguns sistemas superbásicos são mostrados na tabela ao lado.

	H_-
95%DMSO, 5% EtOH, 10^{-2}M KOEt	20,68
90%DMSO, 10% EtOH, 10^{-2}M KOEt	19,68
80%DMSO, 20% EtOH, 10^{-2}M KOEt	18,97
15M KOH, H_2O	18,23
10M KOH, H_2O	16,90
5M KOH, H_2O	15,44

Acidez e Basicidade são conceitos relativos

- Qualquer espécie com um par de elétrons é potencialmente uma base de Lewis
- Tudo depende da avidez por elétrons do ácido.

- **Superelectrophilic Solvation**
  Olah, G. A.; Klumpp, D. A.;
  Acc. Chem. Res.; **(Article); 2004**; *37*(4); 211-220. DOI: 10.1021/ar020102p

Troca H-D de H_2O em superácidos

- **Gold, 1976** - RMN ^1H e ^2H

$$D_2O \xrightarrow[SO_2ClF/SO_2]{FSO_3H.SbF_5} HD_2O^+$$

$(H_o = -21.5)$

Não há troca

- **Olah, 1986** - RMN ^{17}O

$$D_2{}^{17}O \xrightarrow[SO_2,\ -78^oC]{HF.SbF_5} HD_2{}^{17}O^+ \substack{\longrightarrow \\ \longrightarrow} H_3{}^{17}O^+$$

$(H_o = -25 \text{ a } -28)$

Há troca

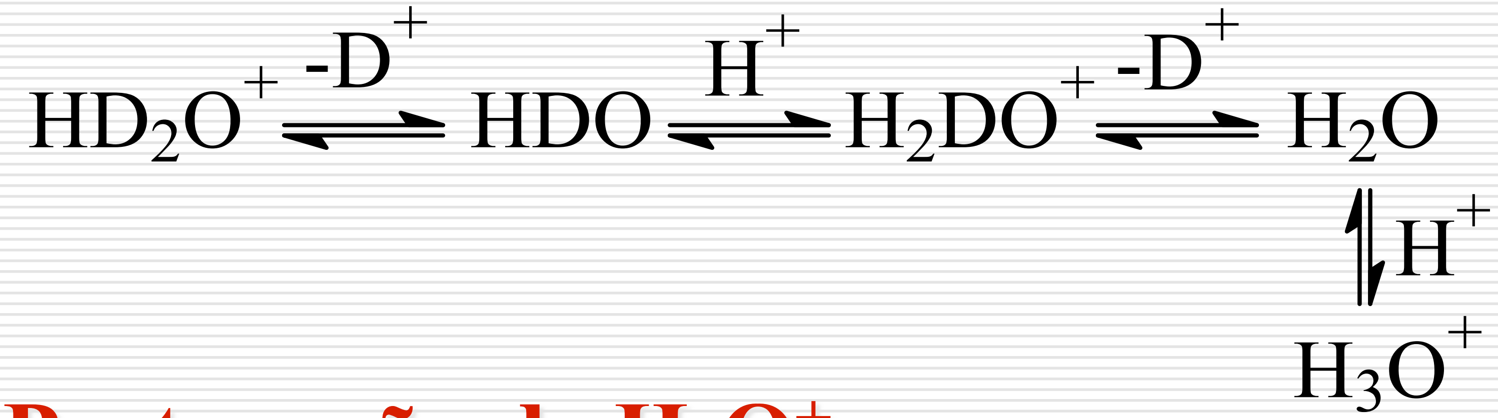
Troca H-D de H_2O em superácidos com H_o entre -25 e -28

↑ acidez ↑ velocidade troca H-D

(↓ H_o)

Mecanismos Possíveis

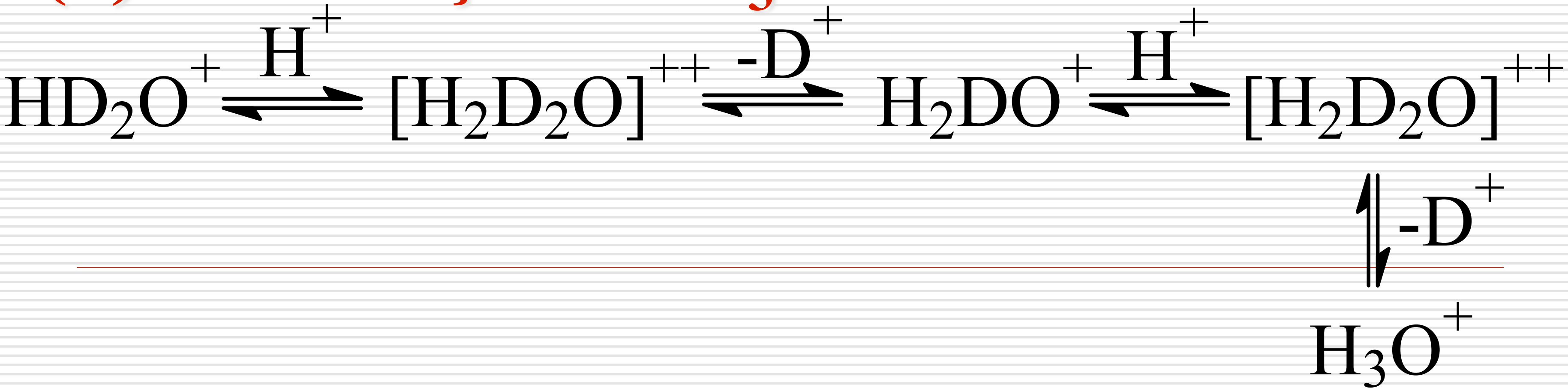
(a) Protonação-desprotonação



$$HD_2O^+ \xrightleftharpoons{-D^+} HDO \xrightleftharpoons{H^+} H_2DO^+ \xrightleftharpoons{-D^+} H_2O$$

$$H_2O \xrightleftharpoons{H^+} H_3O^+$$

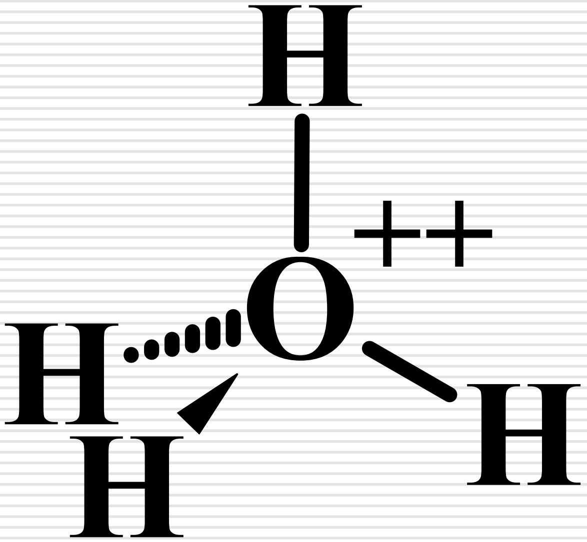
(b) Protonação de H_3O^+



$$HD_2O^+ \xrightleftharpoons{H^+} [H_2D_2O]^{++} \xrightleftharpoons{-D^+} H_2DO^+ \xrightleftharpoons{H^+} [H_2D_2O]^{++}$$

$$[H_2D_2O]^{++} \xrightleftharpoons{-D^+} H_3O^+$$

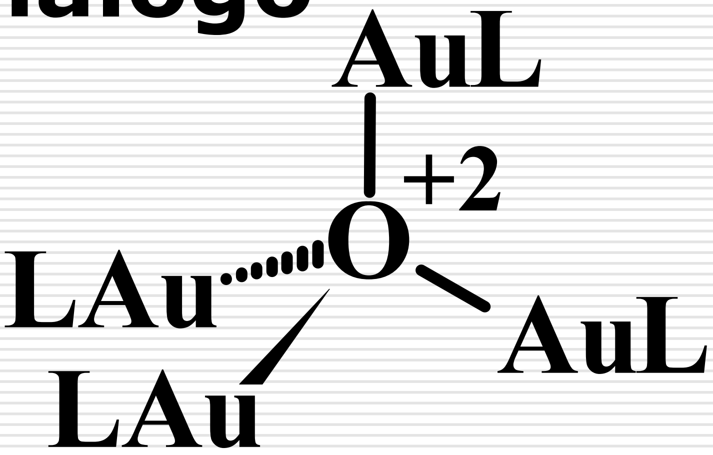
Água diprotonada?!



- É um intermediário (cálculos *ab initio*)
  - barreira desprotonação = 38.2 kcal/mol
  - ΔGº = -60.4 kcal/mol

Água diprotonada?! (Cont.)

- **Schmidbaur, 1995 - síntese de análogo**



$L = Ph_3P$

Au^+ é isolobal a H^+

- **Olah, 1988 - Estudo do H_4S^{++}**
  - Mesmas observações para DH_2S^+

Outros R_3X^+ (X=O, S, Se, Te)

- **Laali, 1987** - **R_3X^+ é muito ativado em presença de superácidos**

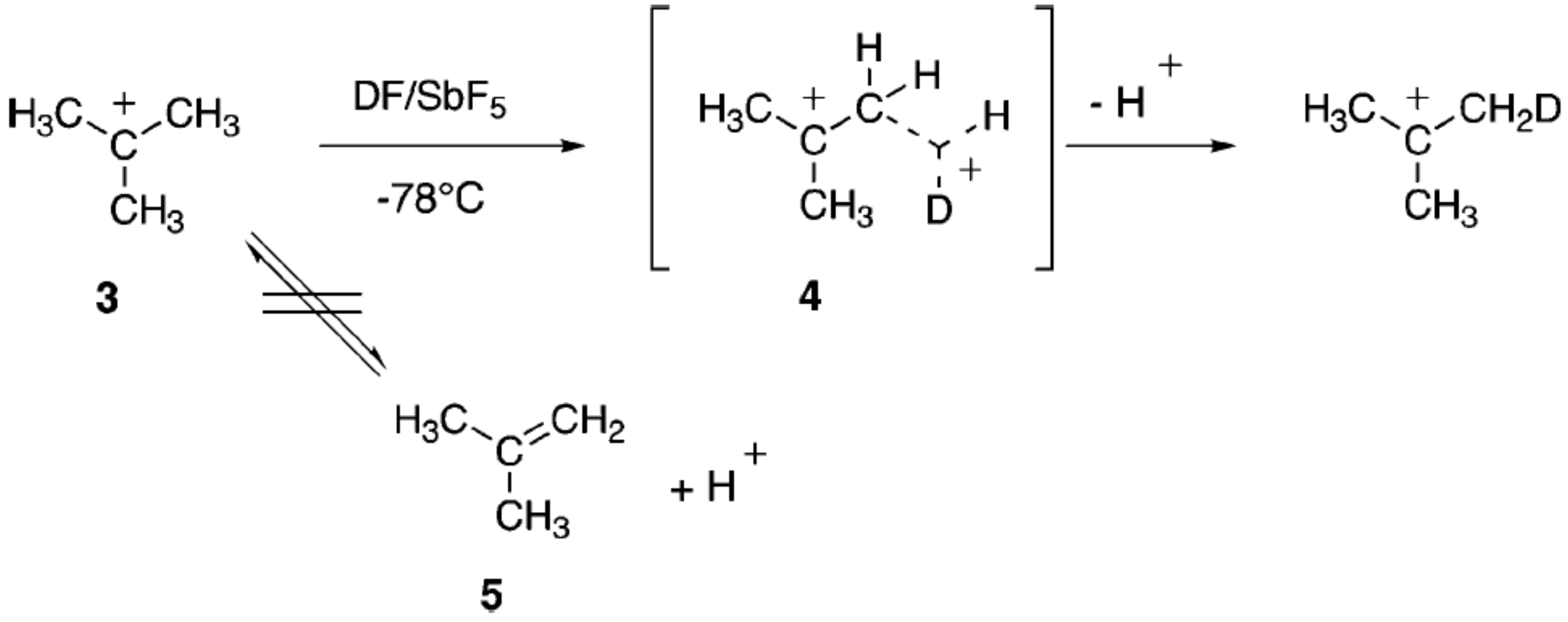
$$R_3X^+ \overset{H^+}{\rightleftarrows} R_3XH^{++} \xrightarrow[-H^+]{ArH} ArR + R_2XH^+$$

- **Olah, 1990** - **fácil redução de MeOH por H_2 em superácidos**

$$CH_3OH_2^+ \overset{H^+}{\rightleftarrows} CH_3OH_3^{++} \xrightarrow[-H^+]{H_2} CH_4 + H_3O^+$$

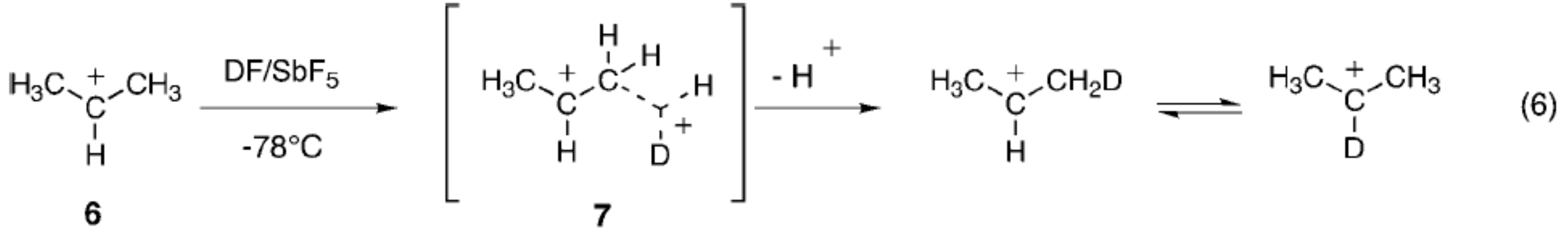
Troca H-D em Íons Carbênio

- **Olah, Prakash, Hartz, Rasul, 1993/1994** – **protonação de íons carbênios**

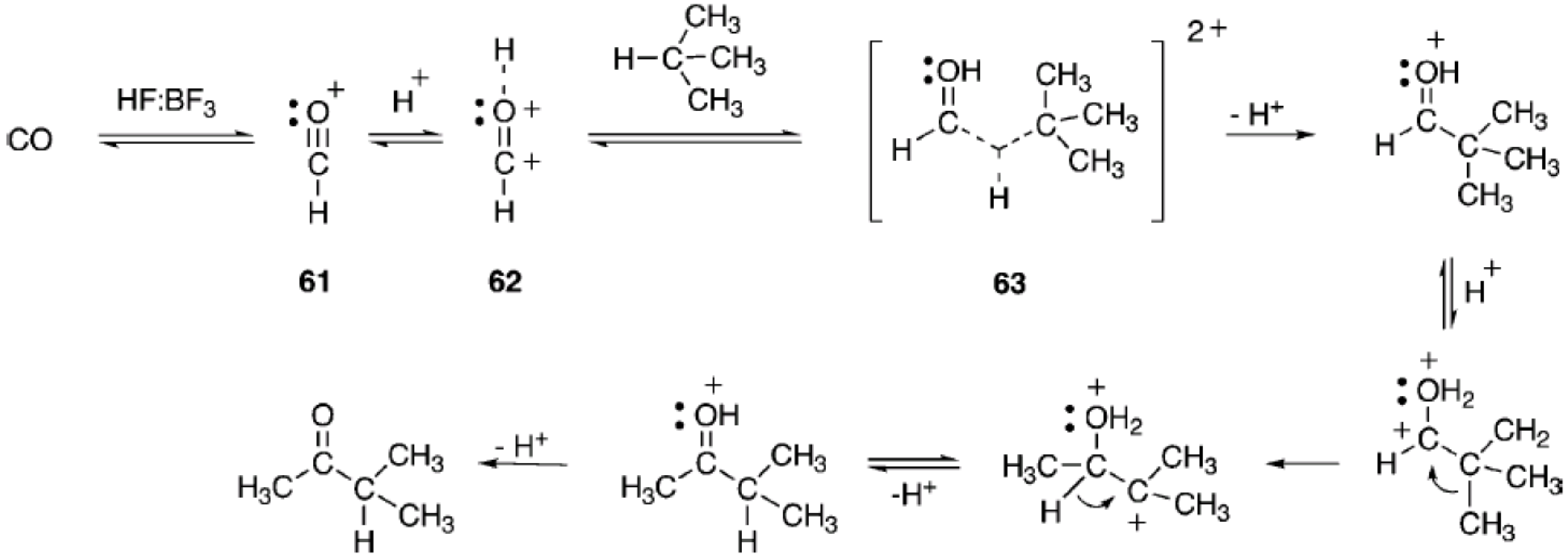


Troca H-D em Íons Carbênio

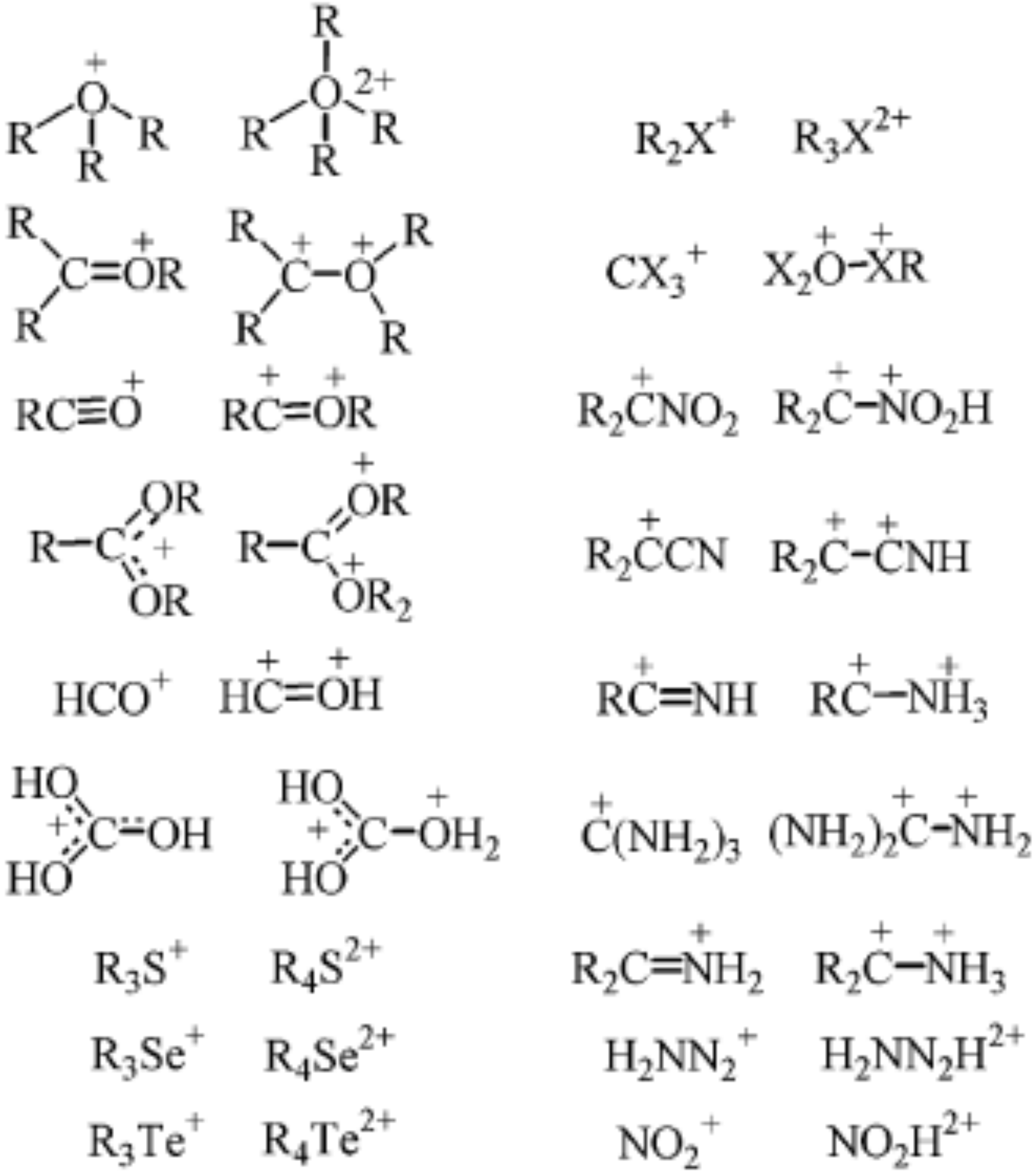
- **Olah, Prakash, Hartz, Rasul 1994**
  - **5% de troca H-D após 72h a -78ºC**



■ Olah, Esteves, Mathew, Prakash 2001



Supereletrófilos



Limites de Acidez-Basicidade

- Em tese

-50 **+50**

- Na prática

-25 **+25**

Estrutura de Raios X de alguns Intermediários reativos

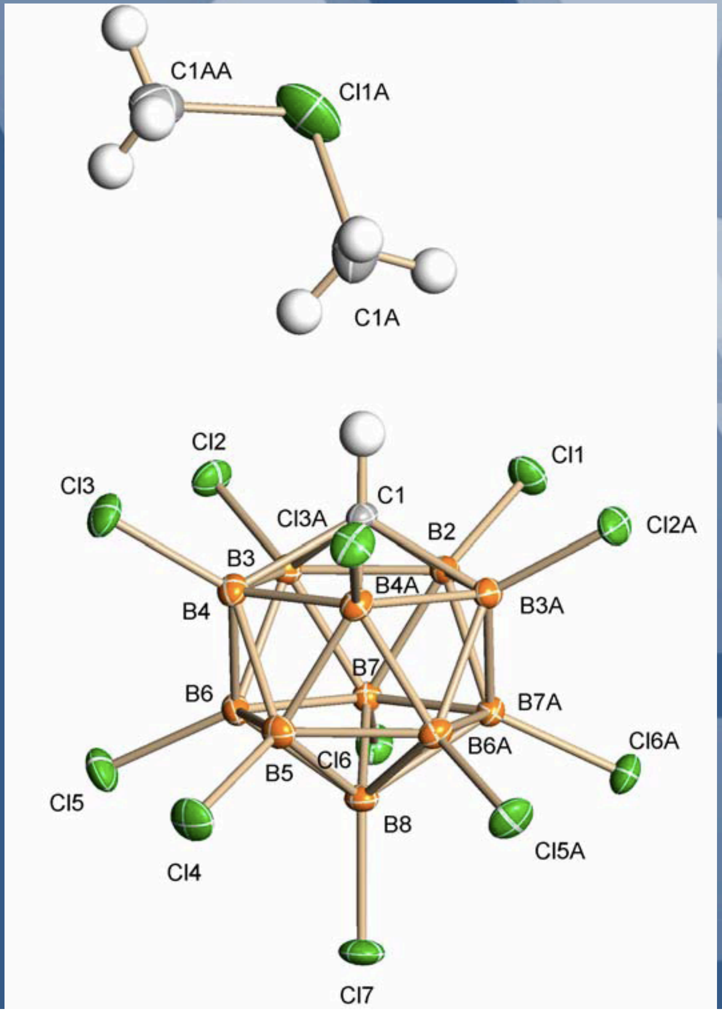
institutodequímica
Universidade Federal do Rio de Janeiro

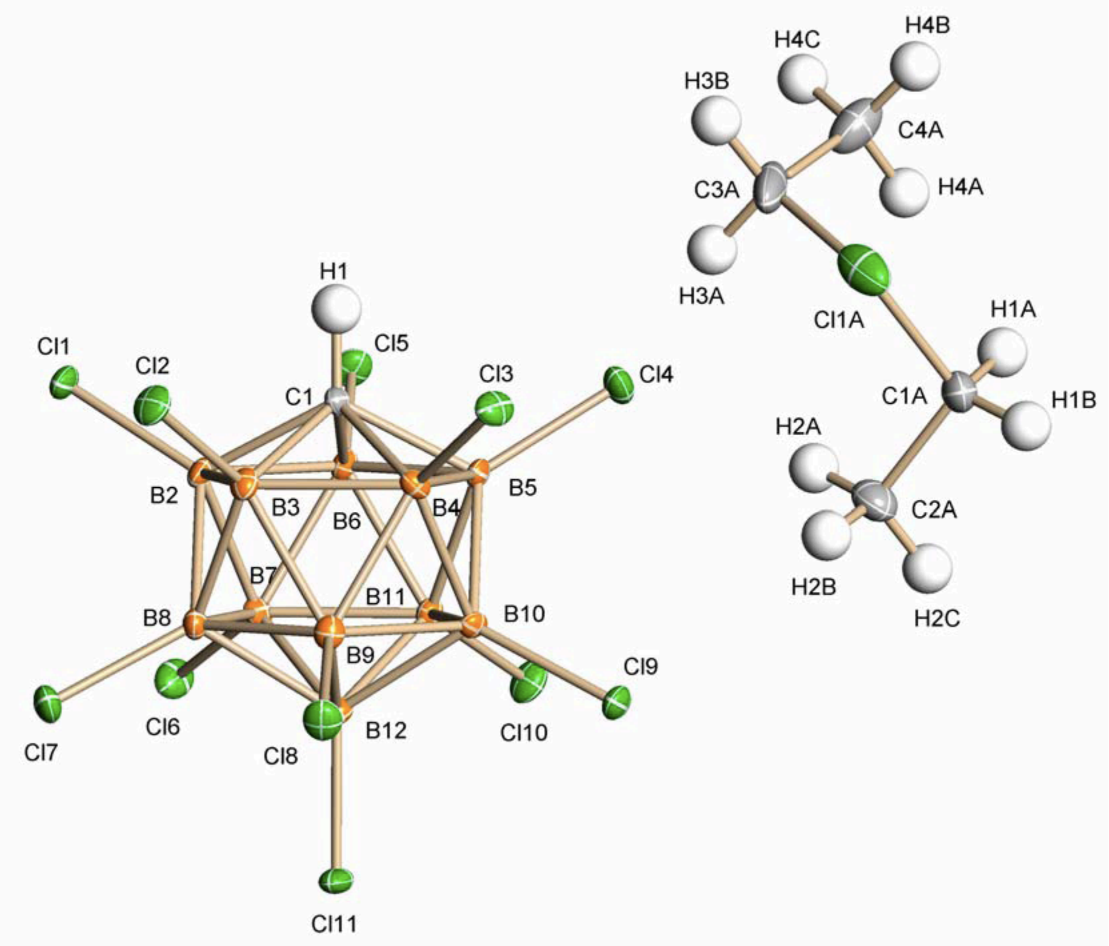
www.iq.ufrj.br
Tel:. 2562-7001 2562-7002

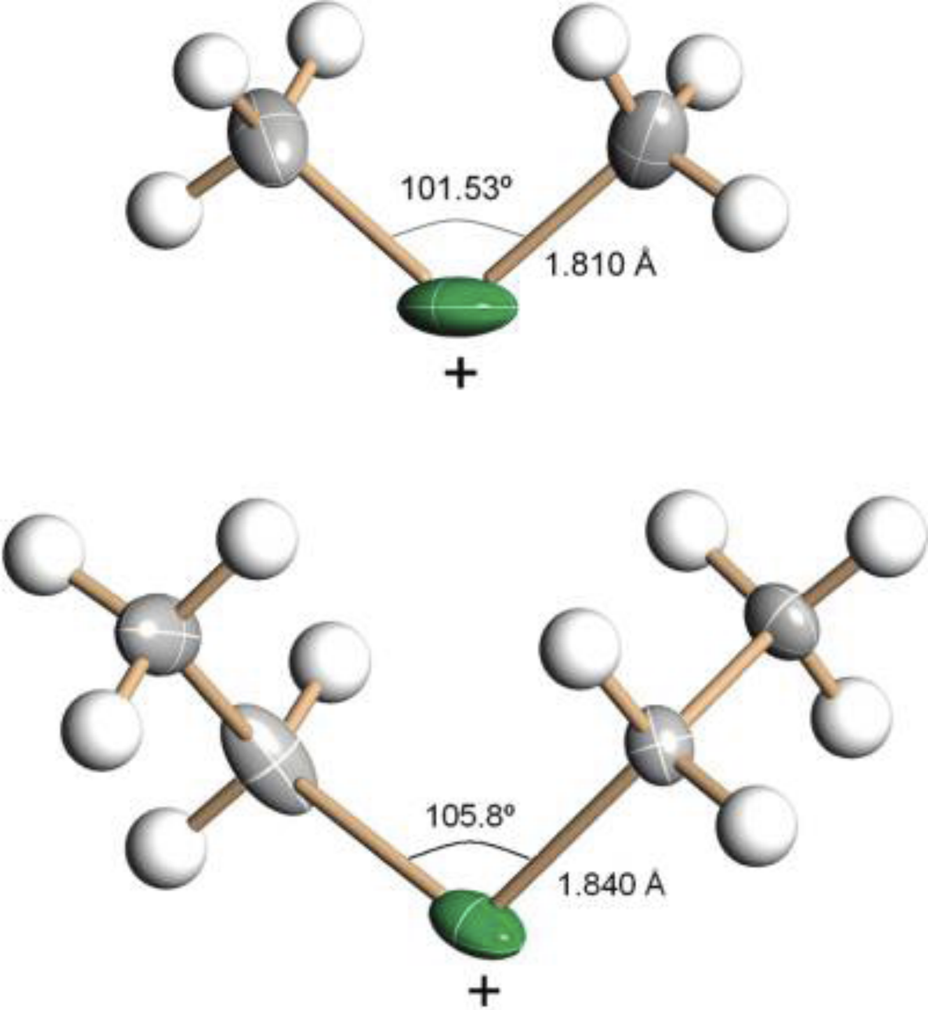
Estrutura de Raios X de alguns Intermediários reativos

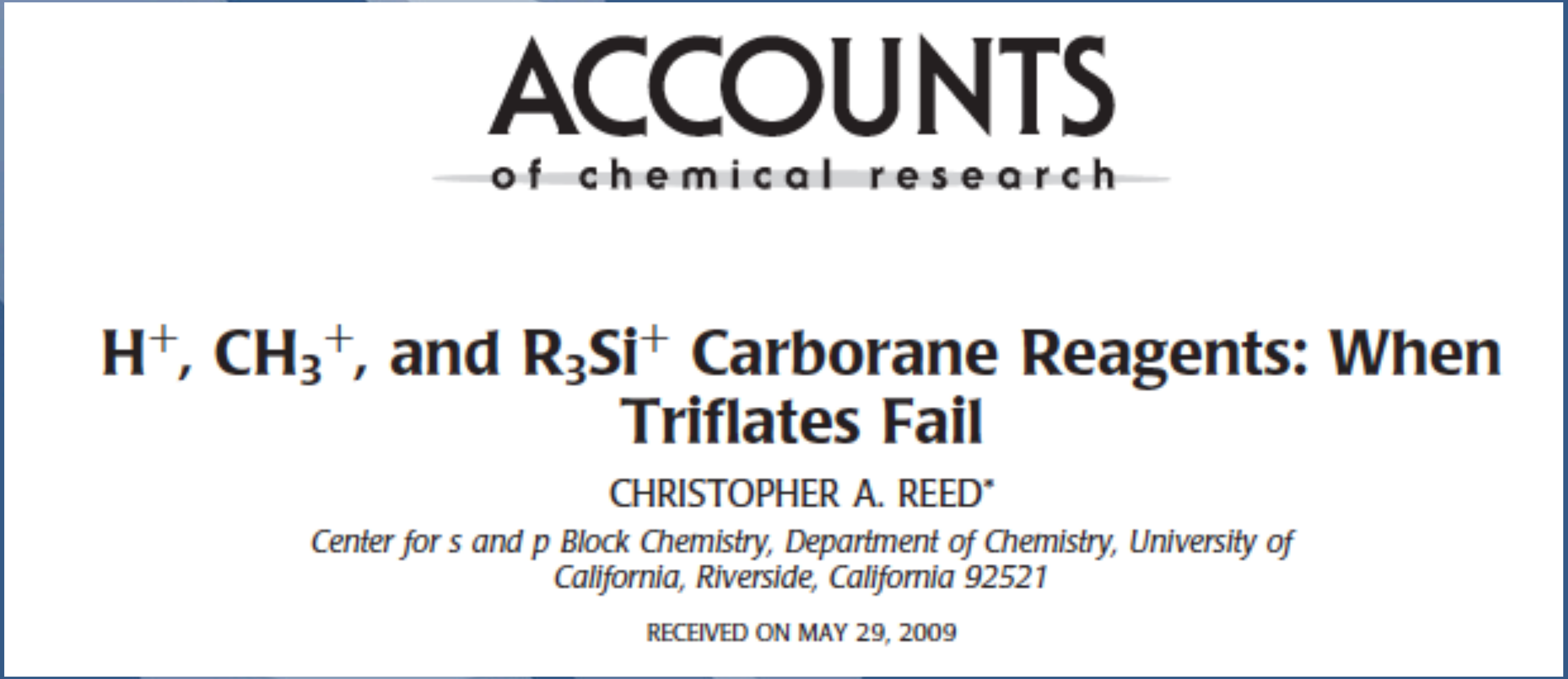
- Íons clorônio

Stoyanov, Stoyanova, Tham, Reed
J. Am. Chem. Soc., 2010, 132 (12), pp 4062–4063
DOI: 10.1021/ja100297b






101.53º
1.810 Å
+
105.8º
1.840 Å
+



ACCOUNTS
of chemical research

H^+, CH_3^+, and R_3Si^+ Carborane Reagents: When Triflates Fail

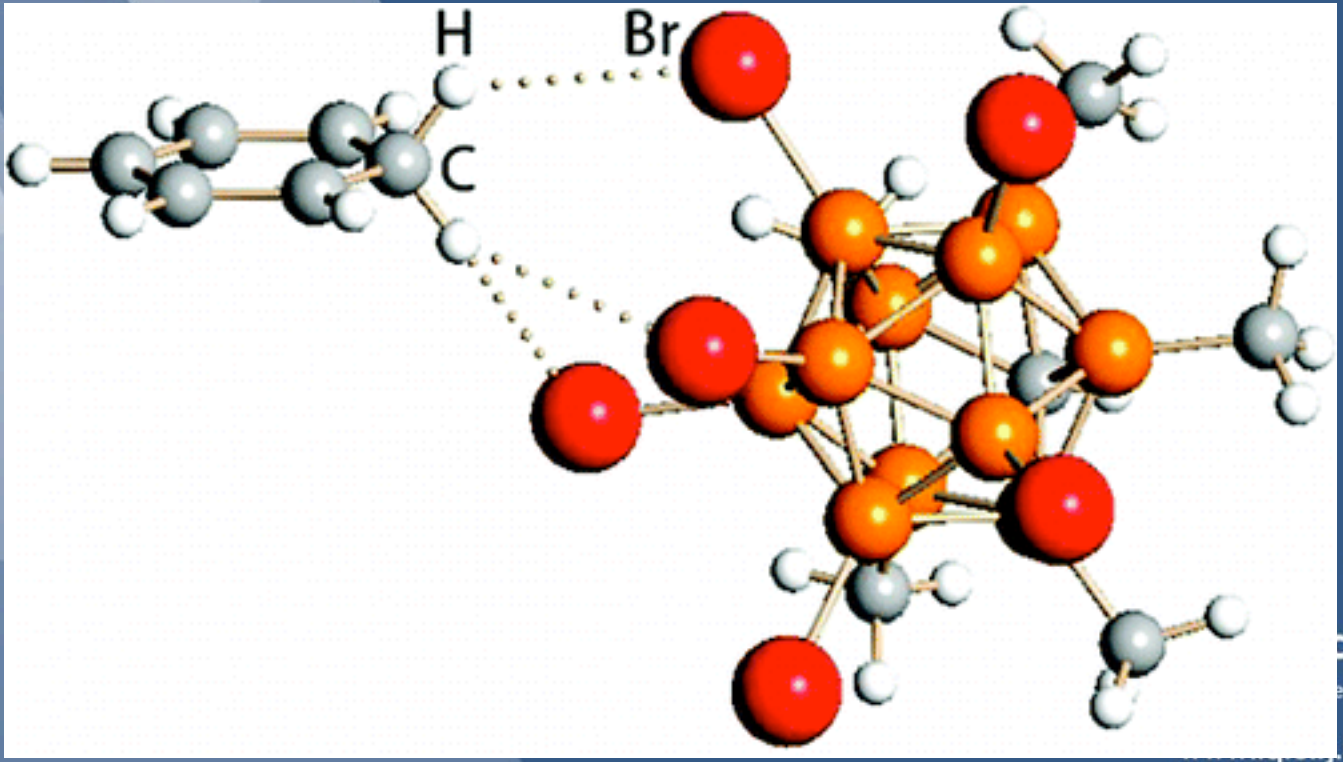
CHRISTOPHER A. REED*
Center for s and p Block Chemistry, Department of Chemistry, University of California, Riverside, California 92521

RECEIVED ON MAY 29, 2009

10.1021/ar900159e

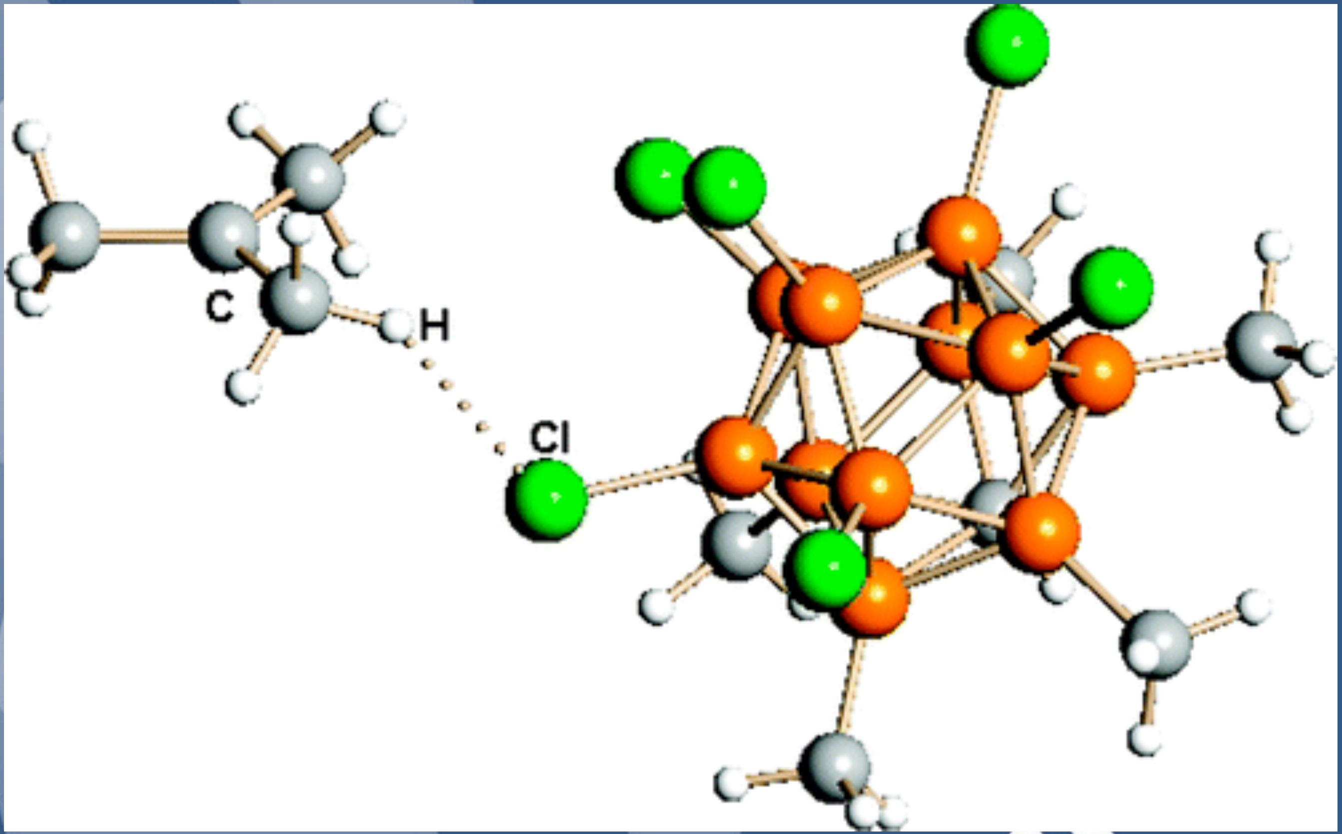
Benzeno protonado: DRX

- $[C_6H_7][CHB_{11}Me_5Br_6]$

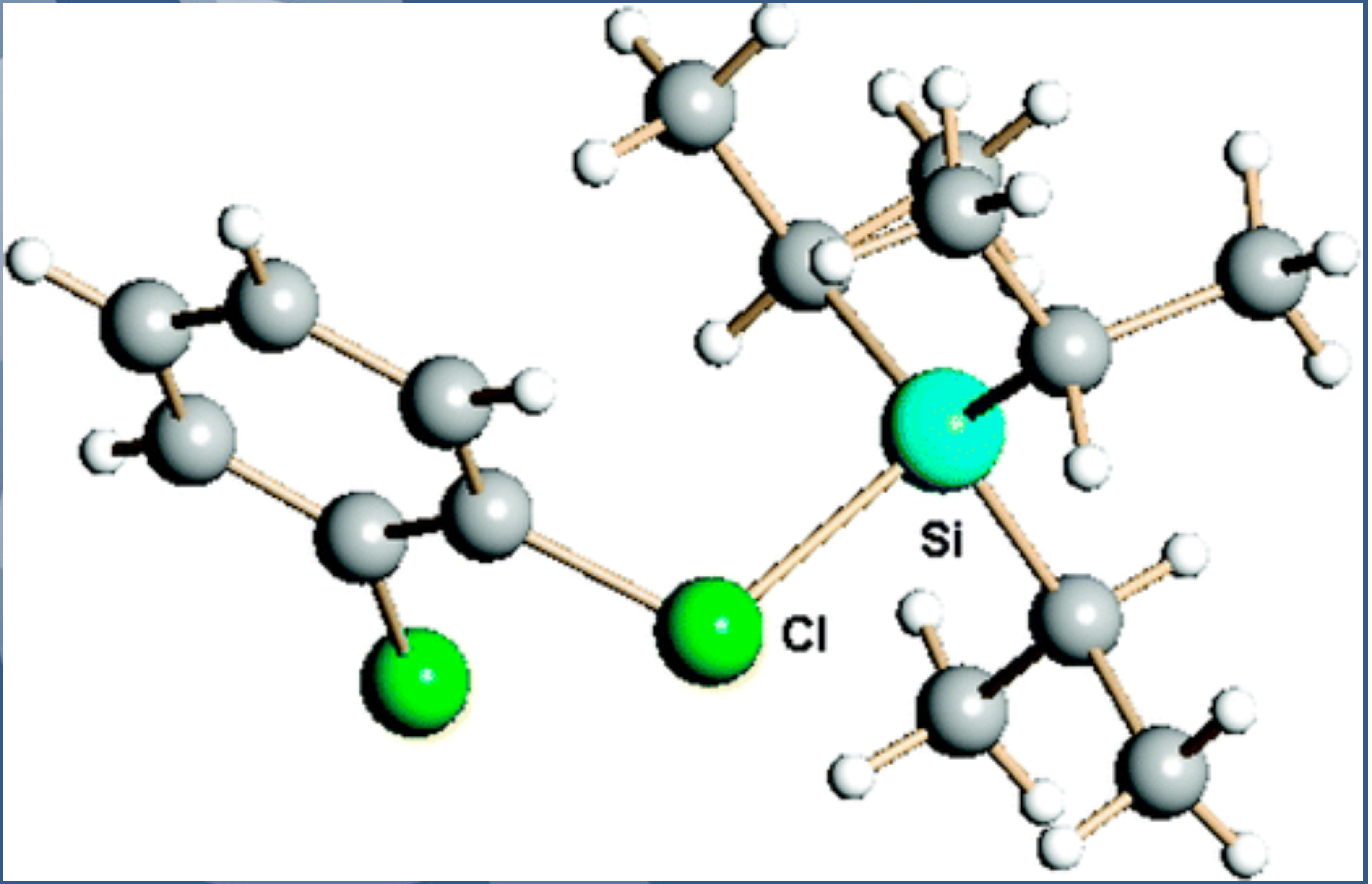


10.1021/ar900159e

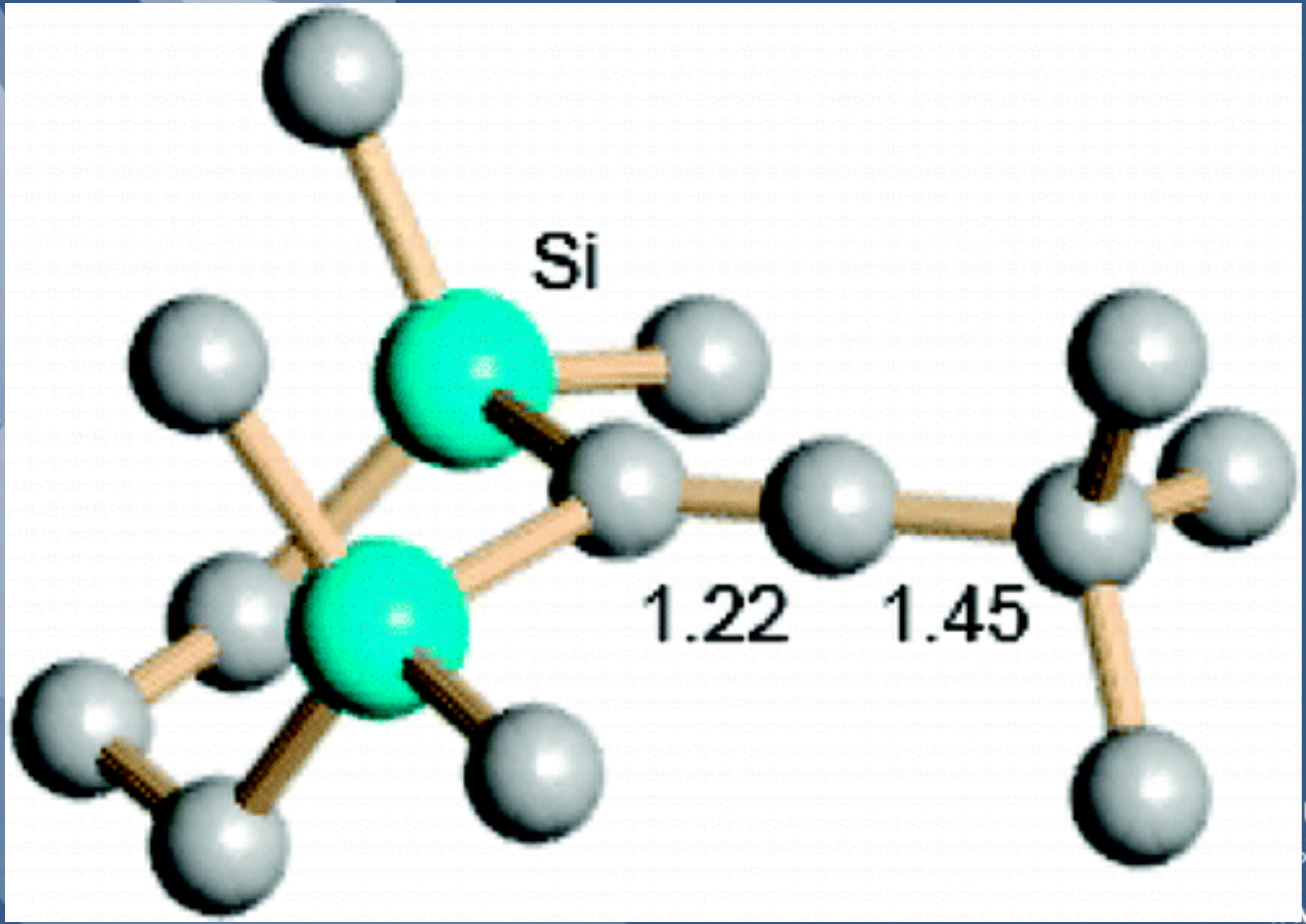
Cátion t-butila: DRX



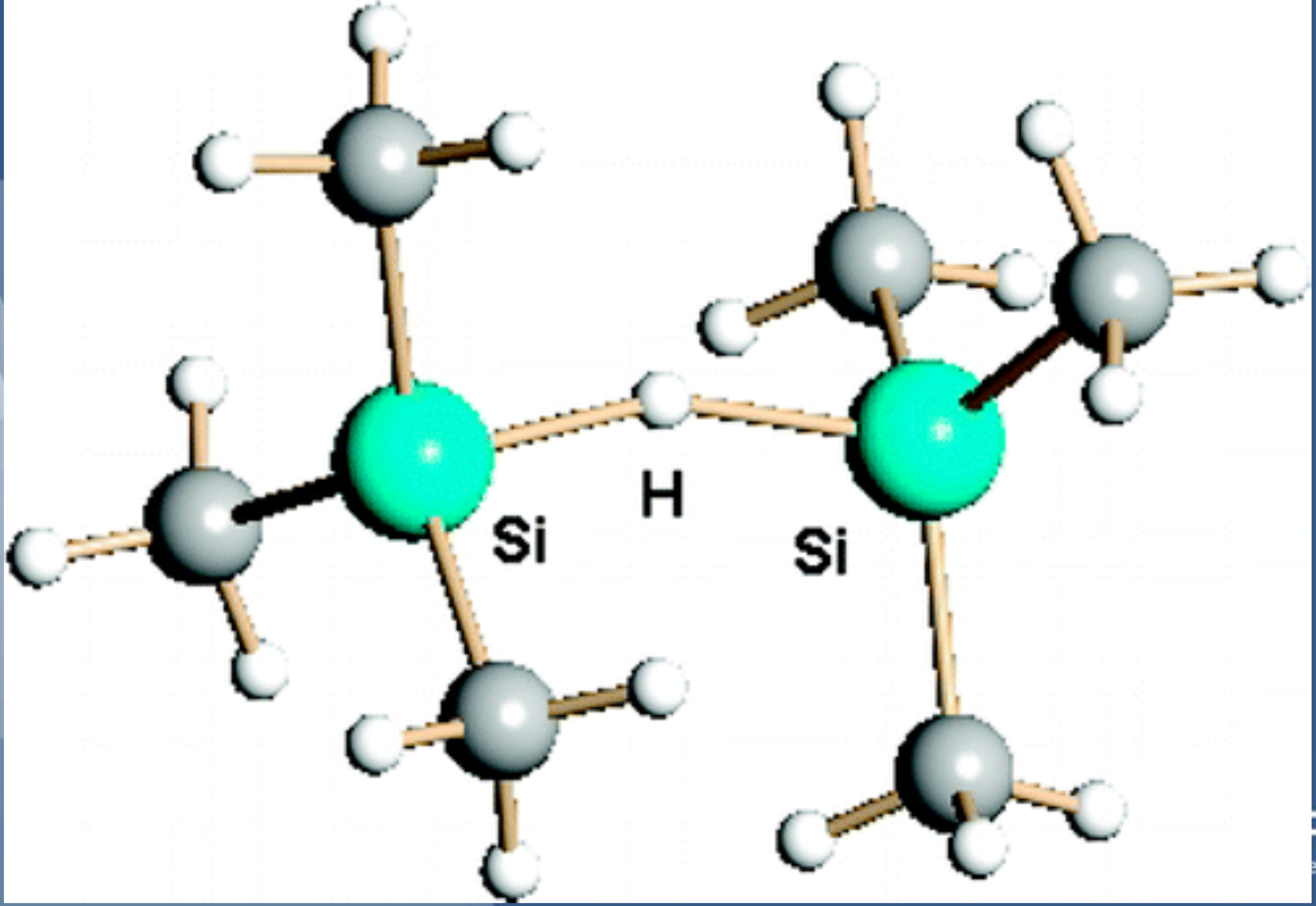
Cátion silênios (R_3Si^+): DRX



Carbênio vinílico β-estabilizado por Silício: DRX



Ligação μ: DRX



Substituição Eletrofílica Aromática

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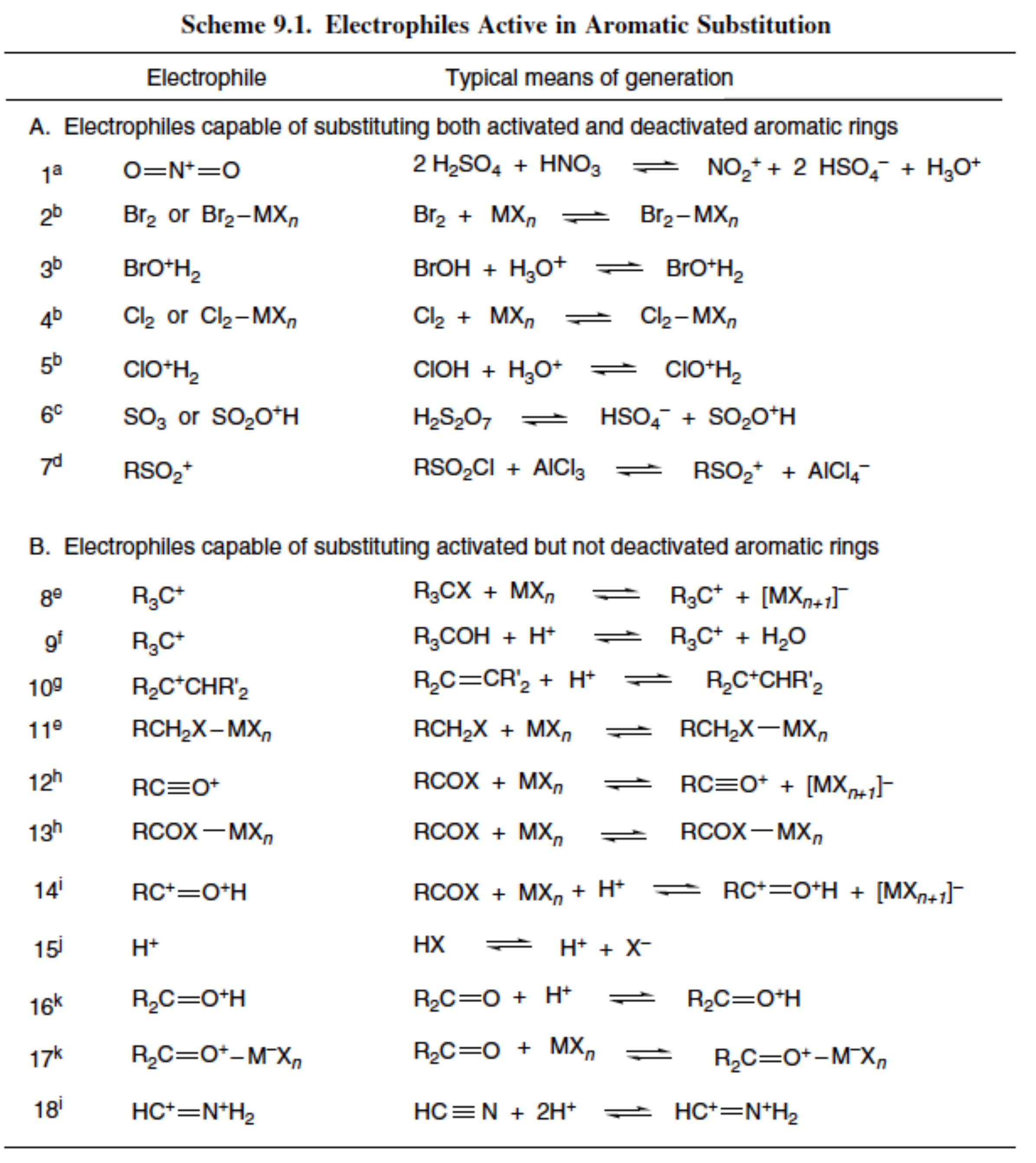
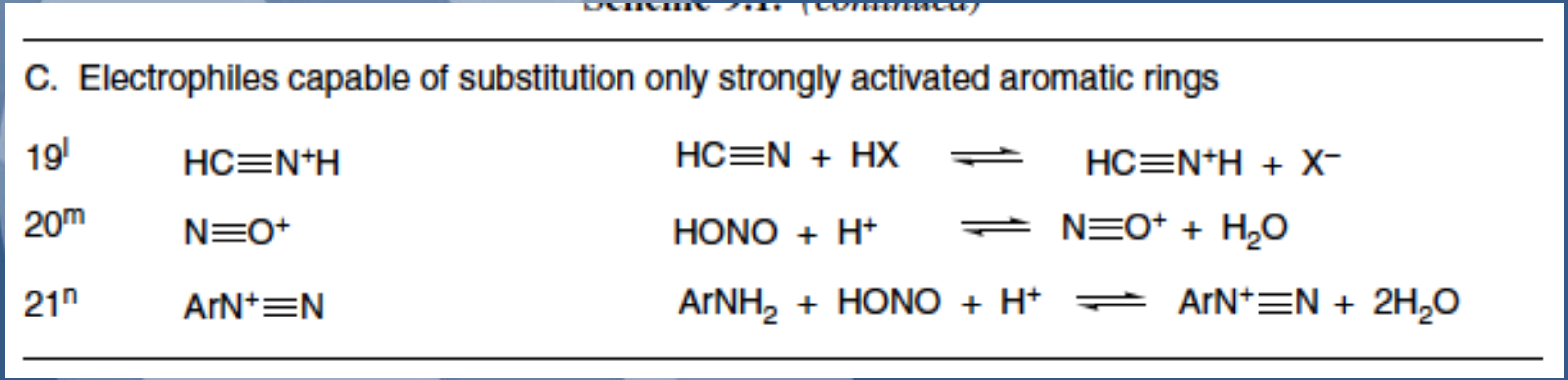


Scheme 9.1. Electrophiles Active in Aromatic Substitution

	Electrophile	Typical means of generation
A. Electrophiles capable of substituting both activated and deactivated aromatic rings		
1[a]	$O{=}N^+{=}O$	$2\,H_2SO_4 + HNO_3 \rightleftharpoons NO_2^+ + 2\,HSO_4^- + H_3O^+$
2[b]	Br_2 or $Br_2{-}MX_n$	$Br_2 + MX_n \rightleftharpoons Br_2{-}MX_n$
3[b]	BrO^+H_2	$BrOH + H_3O^+ \rightleftharpoons BrO^+H_2$
4[b]	Cl_2 or $Cl_2{-}MX_n$	$Cl_2 + MX_n \rightleftharpoons Cl_2{-}MX_n$
5[b]	ClO^+H_2	$ClOH + H_3O^+ \rightleftharpoons ClO^+H_2$
6[c]	SO_3 or SO_2O^+H	$H_2S_2O_7 \rightleftharpoons HSO_4^- + SO_2O^+H$
7[d]	RSO_2^+	$RSO_2Cl + AlCl_3 \rightleftharpoons RSO_2^+ + AlCl_4^-$
B. Electrophiles capable of substituting activated but not deactivated aromatic rings		
8[e]	R_3C^+	$R_3CX + MX_n \rightleftharpoons R_3C^+ + [MX_{n+1}]^-$
9[f]	R_3C^+	$R_3COH + H^+ \rightleftharpoons R_3C^+ + H_2O$
10[g]	$R_2C^+CHR'_2$	$R_2C{=}CR'_2 + H^+ \rightleftharpoons R_2C^+CHR'_2$
11[e]	$RCH_2X{-}MX_n$	$RCH_2X + MX_n \rightleftharpoons RCH_2X{-}MX_n$
12[h]	$RC{\equiv}O^+$	$RCOX + MX_n \rightleftharpoons RC{\equiv}O^+ + [MX_{n+1}]^-$
13[h]	$RCOX{-}MX_n$	$RCOX + MX_n \rightleftharpoons RCOX{-}MX_n$
14[i]	$RC^+{=}O^+H$	$RCOX + MX_n + H^+ \rightleftharpoons RC^+{=}O^+H + [MX_{n+1}]^-$
15[j]	H^+	$HX \rightleftharpoons H^+ + X^-$
16[k]	$R_2C{=}O^+H$	$R_2C{=}O + H^+ \rightleftharpoons R_2C{=}O^+H$
17[k]	$R_2C{=}O^+{-}M^-X_n$	$R_2C{=}O + MX_n \rightleftharpoons R_2C{=}O^+{-}M^-X_n$
18[l]	$HC^+{=}N^+H_2$	$HC{\equiv}N + 2H^+ \rightleftharpoons HC^+{=}N^+H_2$

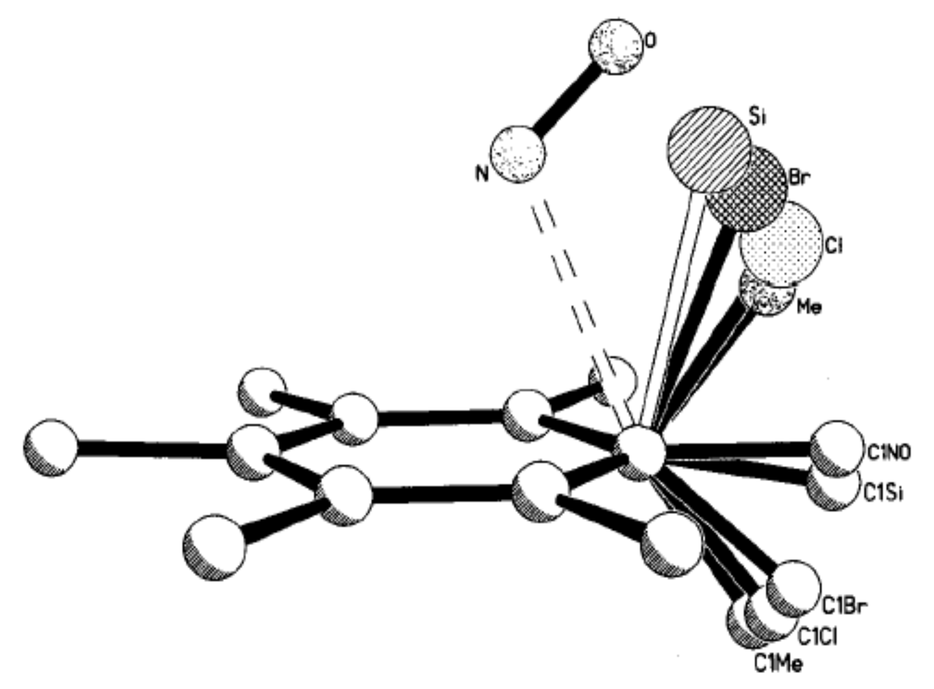


C. Electrophiles capable of substitution only strongly activated aromatic rings

19[l]	$HC{\equiv}N^{+}H$	$HC{\equiv}N + HX \rightleftharpoons HC{\equiv}N^{+}H + X^{-}$
20[m]	$N{\equiv}O^{+}$	$HONO + H^{+} \rightleftharpoons N{\equiv}O^{+} + H_2O$
21[n]	$ArN^{+}{\equiv}N$	$ArNH_2 + HONO + H^{+} \rightleftharpoons ArN^{+}{\equiv}N + 2H_2O$

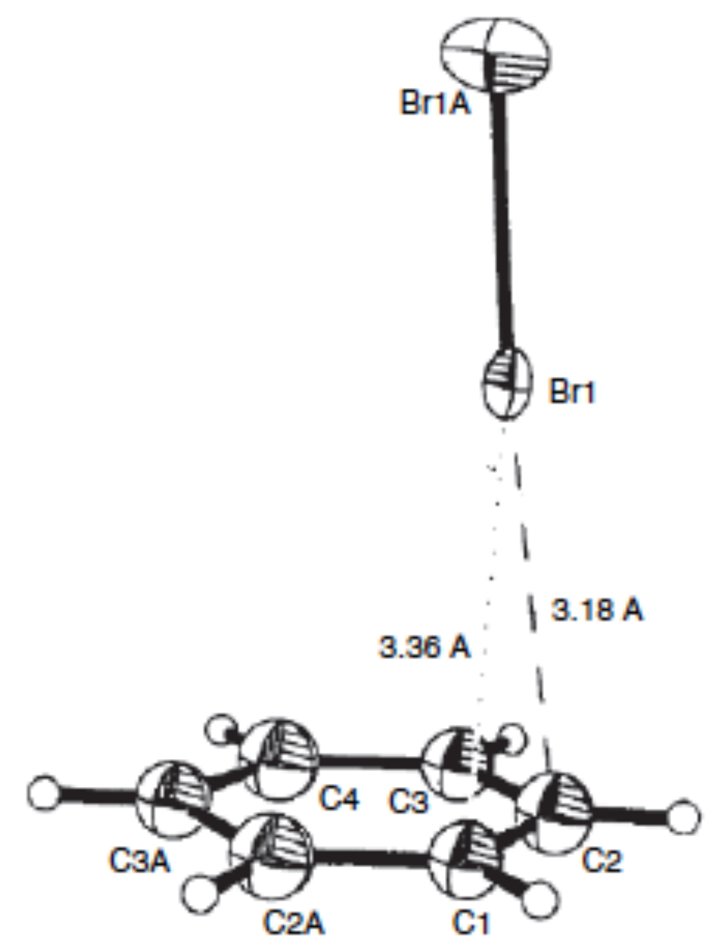
Contínuo σ − π

Complexo π ⟷ **Contínuo σ − π** ⟷ Complexo σ



Kochi, J. K., Hubig, S. M. ***J. Org. Chem***, 65, 21, **2002**, 6807

Complexos pi



A. V. Vasilyev, S. V. Lindeman, and J. K. Kochi, *Chem. Commun., 909 (2001);*
S. V. Rosokha and J. K. Kochi, *J. Org. Chem.,* ***67, 1727 (2002).***

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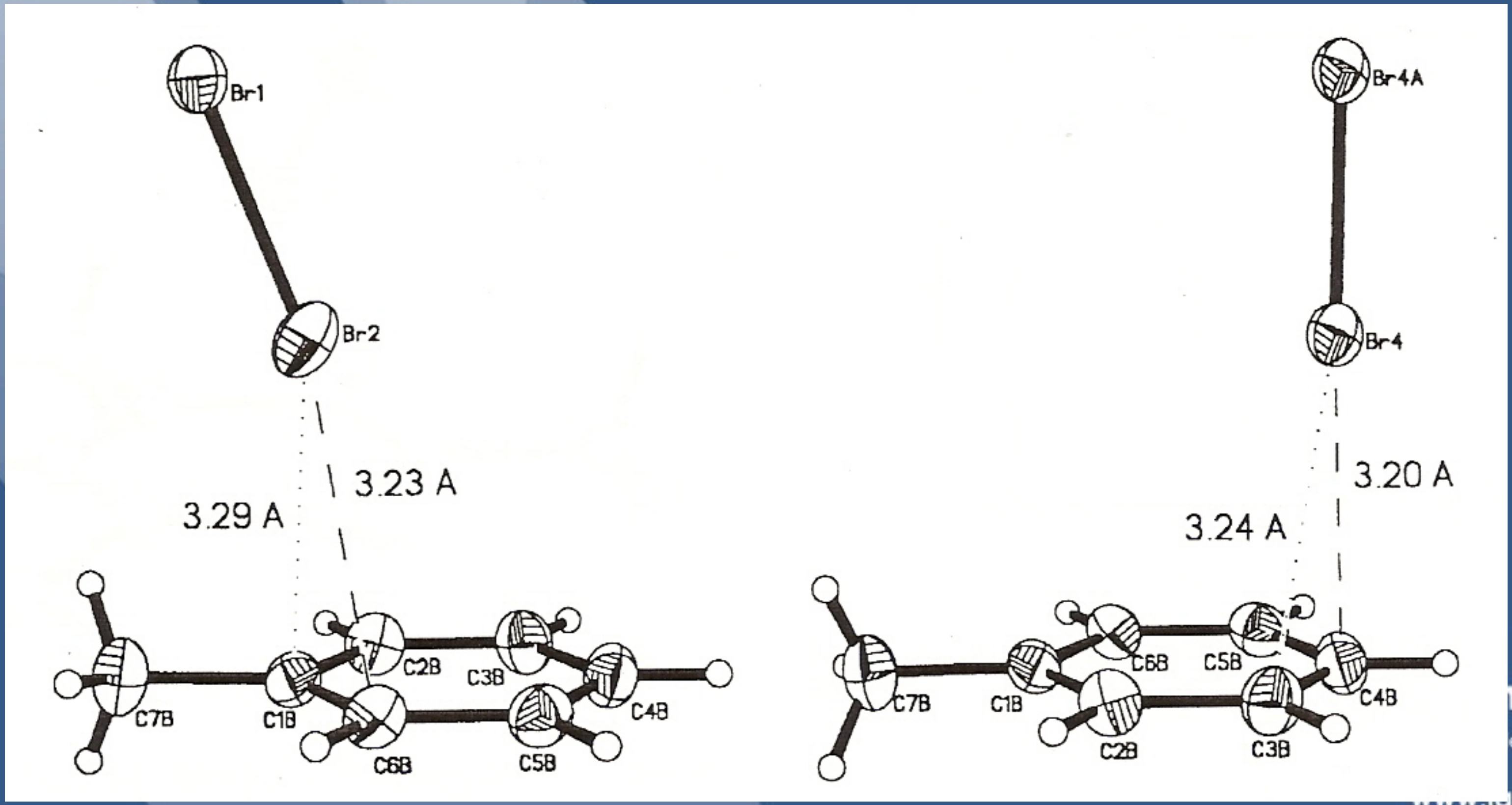
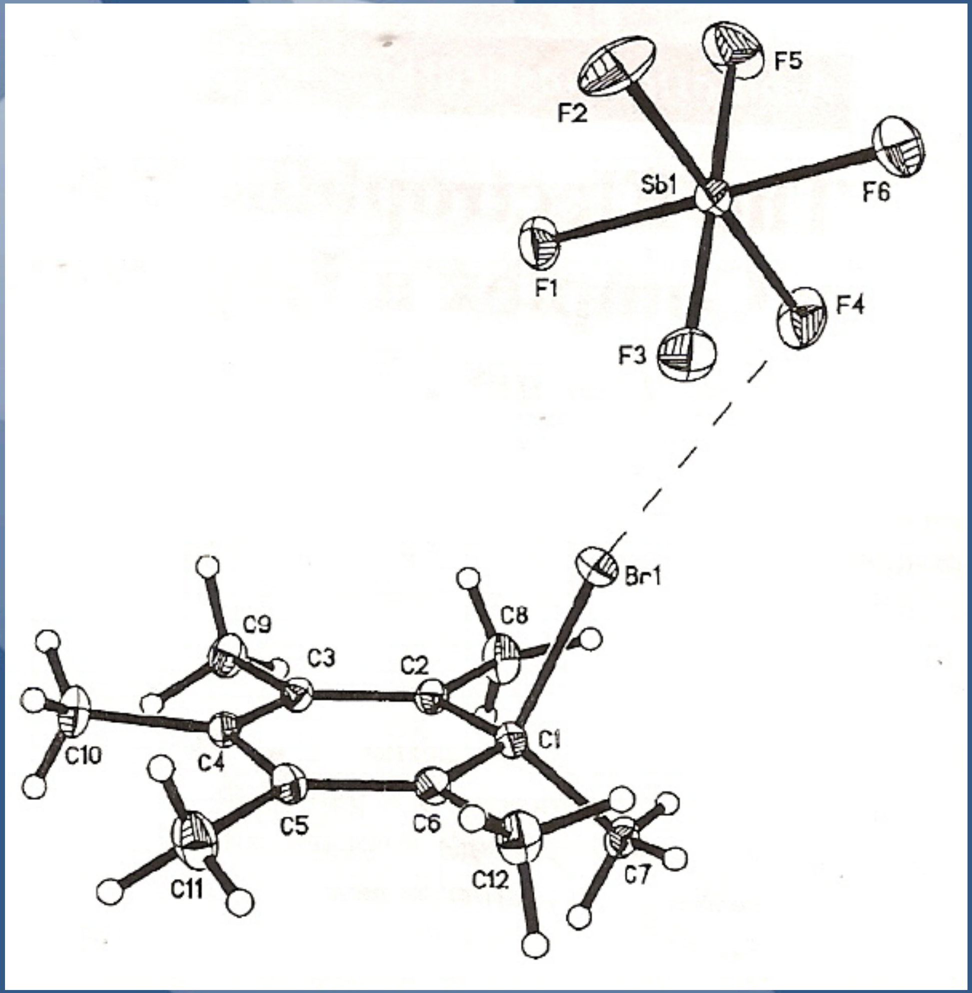
Complexos pi



KOCHI, J. K., VASILYEV A. V., LINDEMAN, S. V., **New J. Chem**. 26, (2002a), 582 – 592.

Complexos sigma



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KOCHI, J. K., VASILYEV A. V., LINDEMAN, S. V., **New J. Chem**. 26, (2002a), 582 – 592.

Complexo pi ou Doador-aceptor?

- NO^+ com mesitileno
- Na verdade é NO com o cation radical do mesitileno

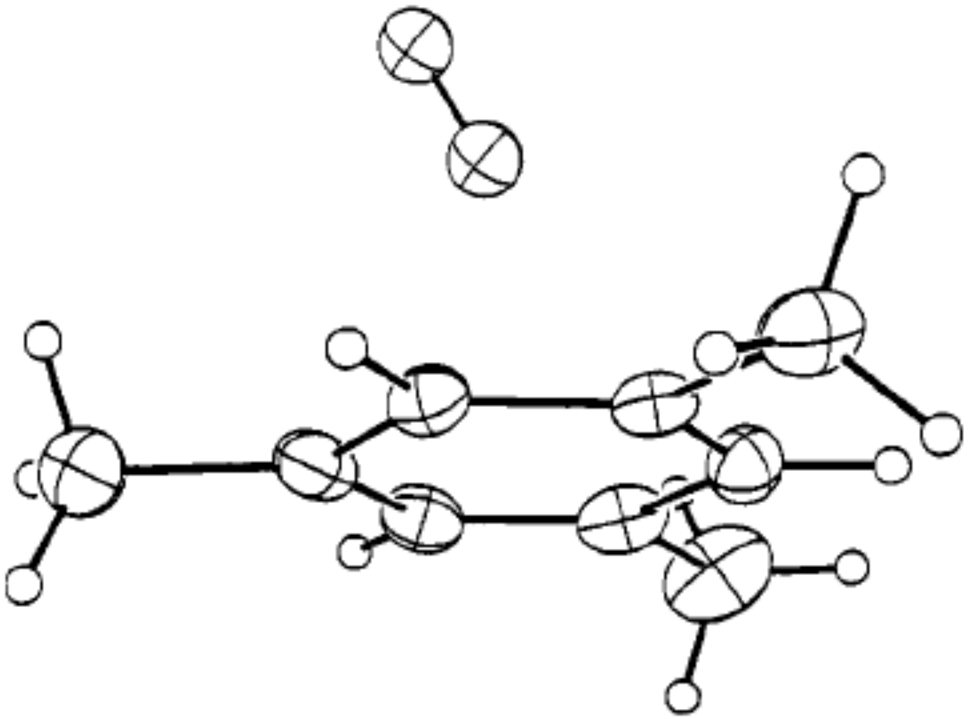

Figure 2. ORTEP diagram of the crystalline 1:1 EDA complex of mesitylene with $NO^+SbCl_6^-$, showing the central location of the NO^+ acceptor over the benzene plane.

E. K. Kim and J. K. Kochi, *J. Am. Chem. Soc.*, ***113, 4962 (1991).***

Espectros

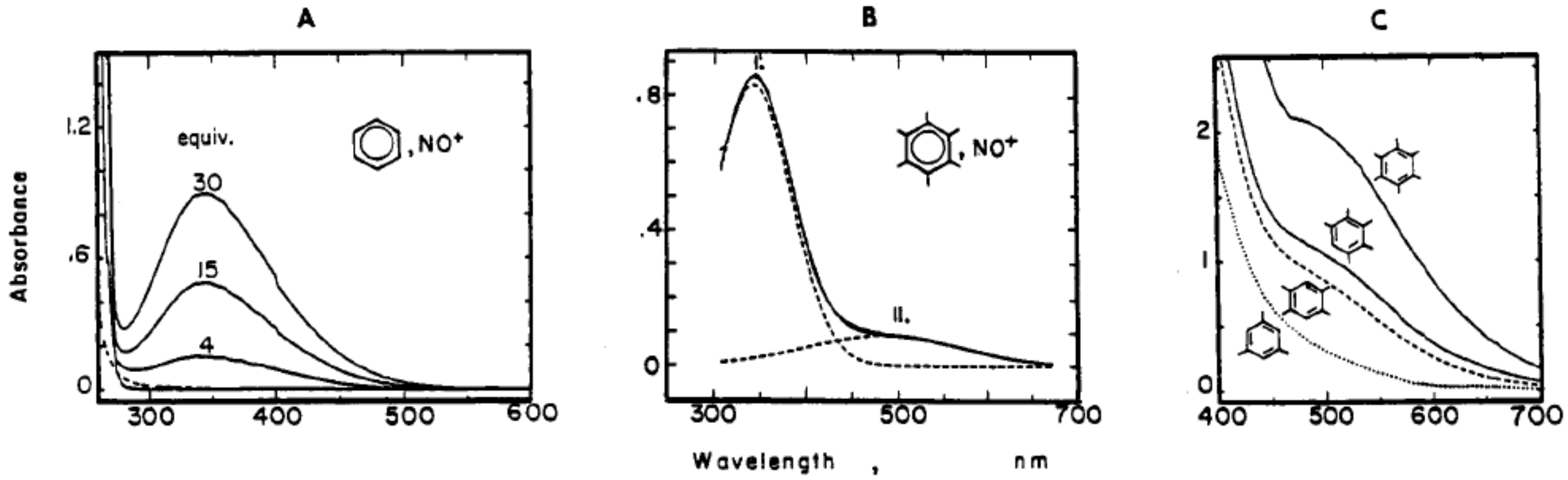

Figure 1. Charge-transfer spectrum of the NO^+ complexes with (A) benzene and (B) hexamethylbenzene in acetonitrile at 25 °C. (C) Bathochromic shift of the low-energy band with increasing donor strength in the order hexamethylbenzene, pentamethylbenzene, durene, and mesitylene, as indicated in nitromethane.

Green Chemistry

- Uso de carbonatos como solventes em síntese orgânica

- **Organic Carbonates as Solvents in Synthesis and Catalysis**
- Benjamin Schffner, Friederike Schffner, Sergey P. Verevkin, and Armin Brner
- **Publication Date (Web):** 29 Mar 2010 (Review)
- **DOI:** 10.1021/cr900393d

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