TÁMOP-4.1.1.F-14/1/KONV-2015-0006
SZTE TTIK, KTCS, 1a) Duális és moduláris képzésfejlesztés a mesterképzéshez

(Fél)kvantitatív szerves kémia 1.

Pálinkó István, egyetemi tanár

SZÉCHENYI 2020
MAGYARORSZÁG KORMÁNYA
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BEFEKTETÉS A JÖVŐBE

Átalakulási mechanizmusok felderítése

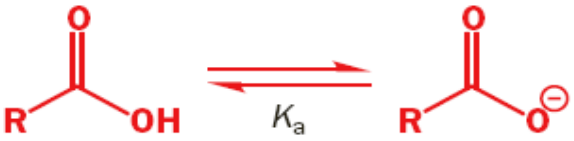
- az elemi reakciók azonosítása
- intermedierek szerekezetének felderítése
- az átmeneti komplex(ek) szerkezete

az elektronküldő, illetve elektronszívó csoportok hatása az átmeneti komplex szerkezetére

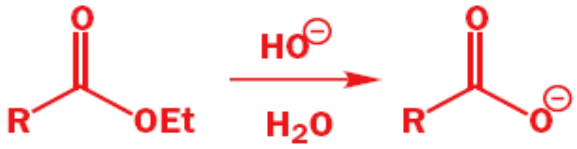
↓

Hammett-összefüggés

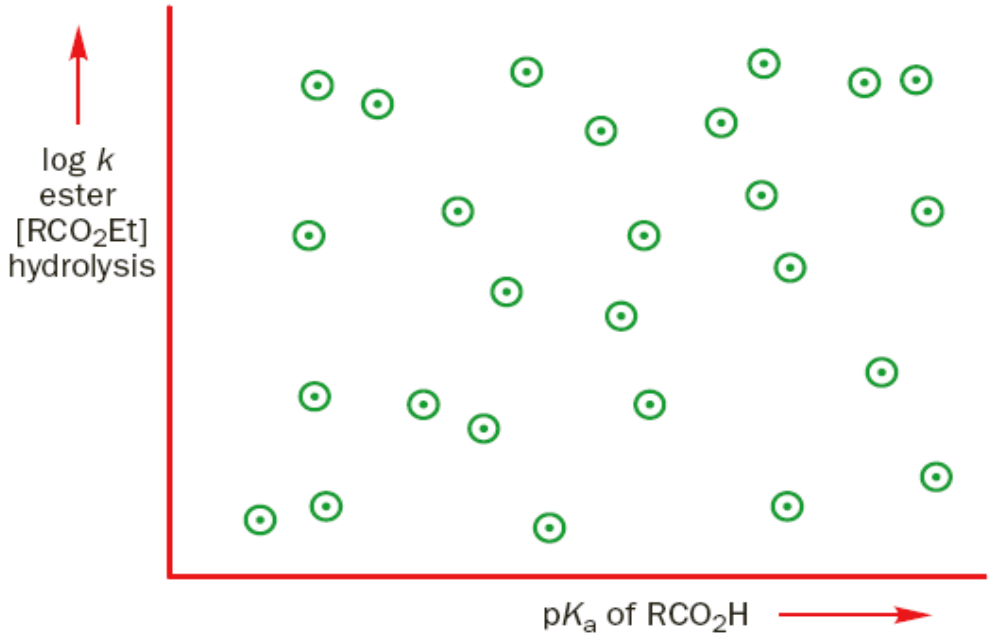
Észterhidrolízis

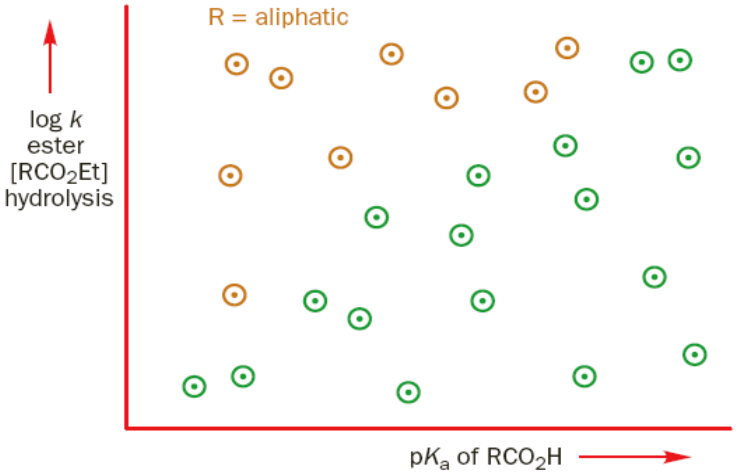


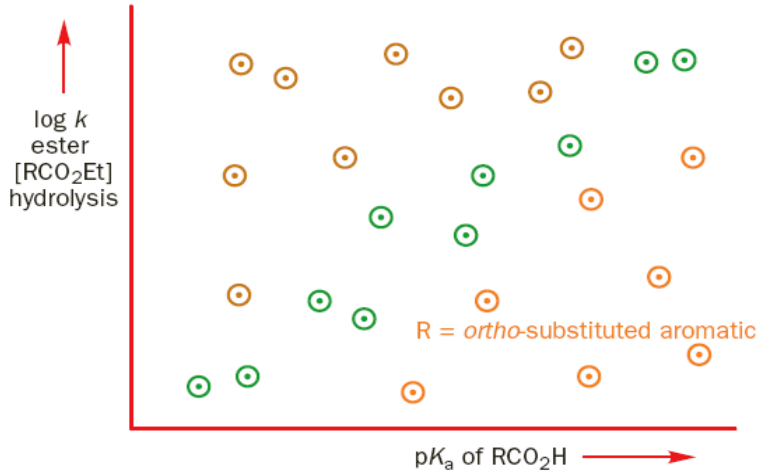
substituent on R is mechanistic probe

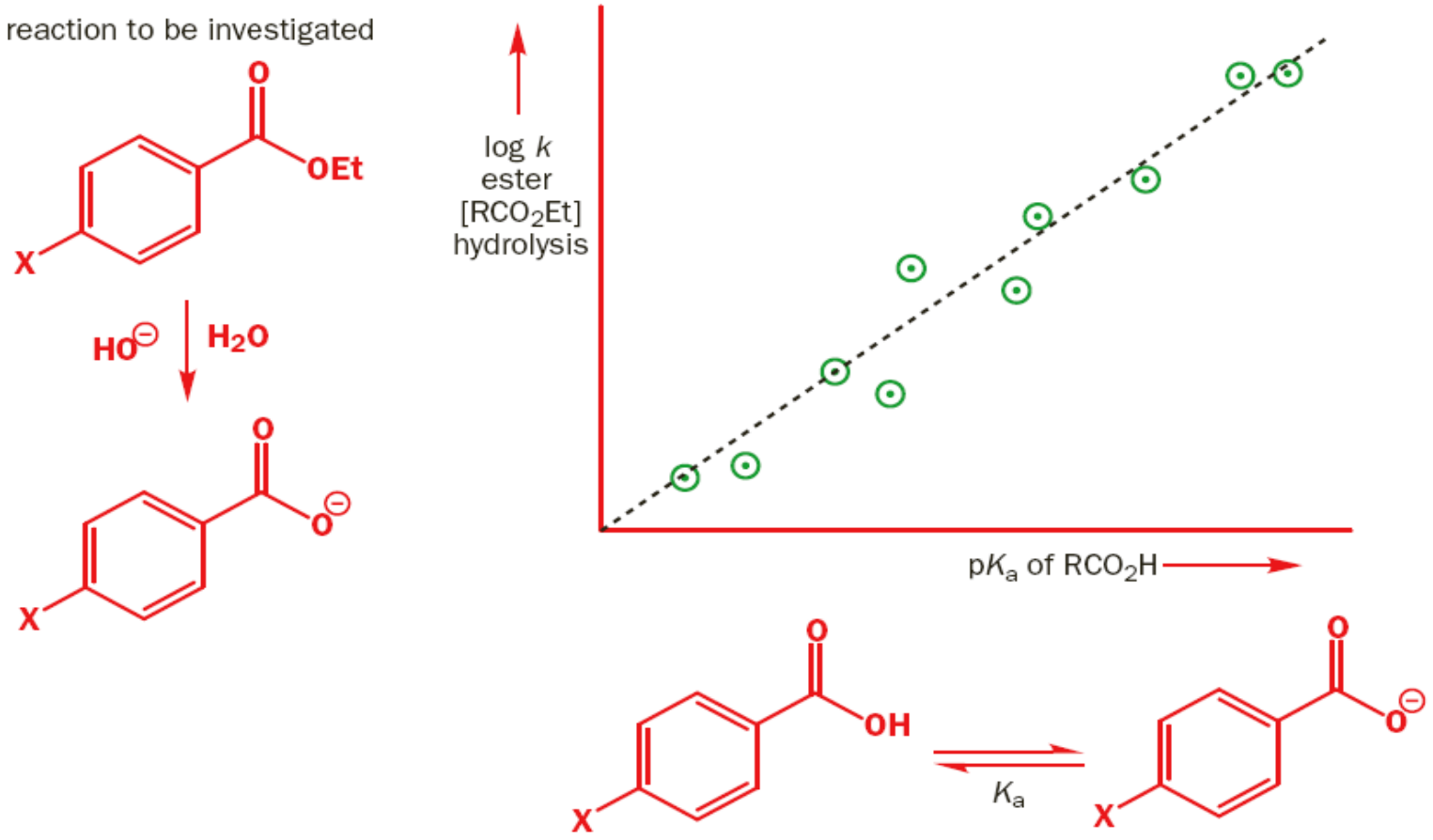


reaction to be investigated



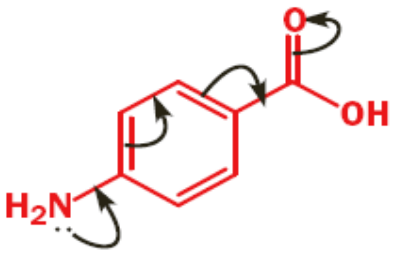

R = aliphatic
log k
ester
[RCO2Et]
hydrolysis
pKa of RCO2H


log k
ester
[RCO2Et]
hydrolysis
R = ortho-substituted aromatic
pKa of RCO2H

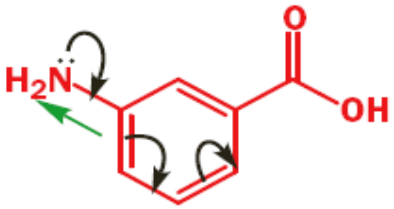

reaction to be investigated
O
OEt
X
HO⊖
H2O
O
O⊖
X
log k
ester
[RCO2Et]
hydrolysis
pKa of RCO2H
O
OH
X
Ka
O
O⊖
X

Substituent, X	pK_a of *p*-XC_6H_4COOH	pK_a of *m*-XC_6H_4COOH
NH_2	4.82	4.20
OCH_3	4.49	4.09
CH_3	4.37	4.26
H	4.20	4.20
F	4.15	3.86
I	3.97	3.85
Cl	3.98	3.83
Br	3.97	3.80
CO_2CH_3	3.75	3.87
$COCH_3$	3.71	3.83
CN	3.53	3.58
NO_2	3.43	3.47

Az elektronszívó, illetve elektronküldő hatás kvalitatív elemzése



strong conjugation
into carbonyl group:



conjugation into ring
not carbonyl group
balances weak effect
of electronegative N:

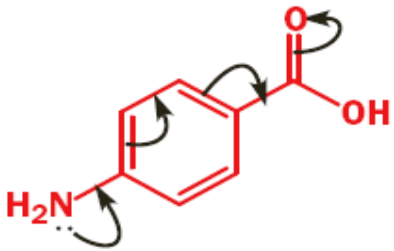
Az elektronszívó, illetve elektronküldő hatás kvantitatív értelmezése

Substituent, X	pK_a of *p*-XC_6H_4COOH	pK_a of *m*-XC_6H_4COOH
NH_2	4.82	4.20
OCH_3	4.49	4.09
CH_3	4.37	4.26
H	4.20	4.20
F	4.15	3.86
I	3.97	3.85
Cl	3.98	3.83
Br	3.97	3.80
CO_2CH_3	3.75	3.87
$COCH_3$	3.71	3.83
CN	3.53	3.58
NO_2	3.43	3.47

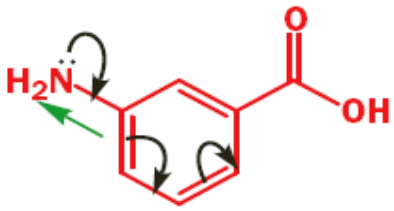
$$\sigma_X = pK_a(C_6H_5COOH) - pK_a(X\text{-}C_6H_5COOH)$$

ez egy definíció

Substituent, X	σ_p	σ_m	Comments
NH_2	–0.62	0.00	groups that donate electrons have negative σ
OCH_3	–0.29	0.11	
CH_3	–0.17	–0.06	
H	0.00	0.00	there are no values for *ortho* substituents
F	0.05	0.34	
I	0.23	0.35	
Cl	0.22	0.37	$\sigma_p < \sigma_m$ for inductive withdrawal
Br	0.23	0.40	
CO_2CH_3	0.45	0.33	
$COCH_3$	0.49	0.37	$\sigma_p > \sigma_m$ for conjugating substituents
CN	0.67	0.62	
NO_2	0.77	0.73	groups that withdraw electrons have positive σ



strong conjugation
into carbonyl group:
large negative σ_p

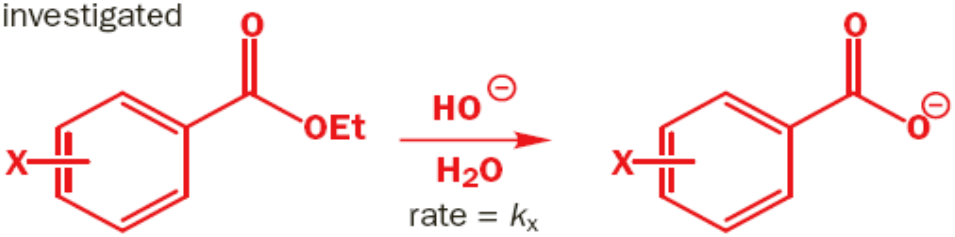


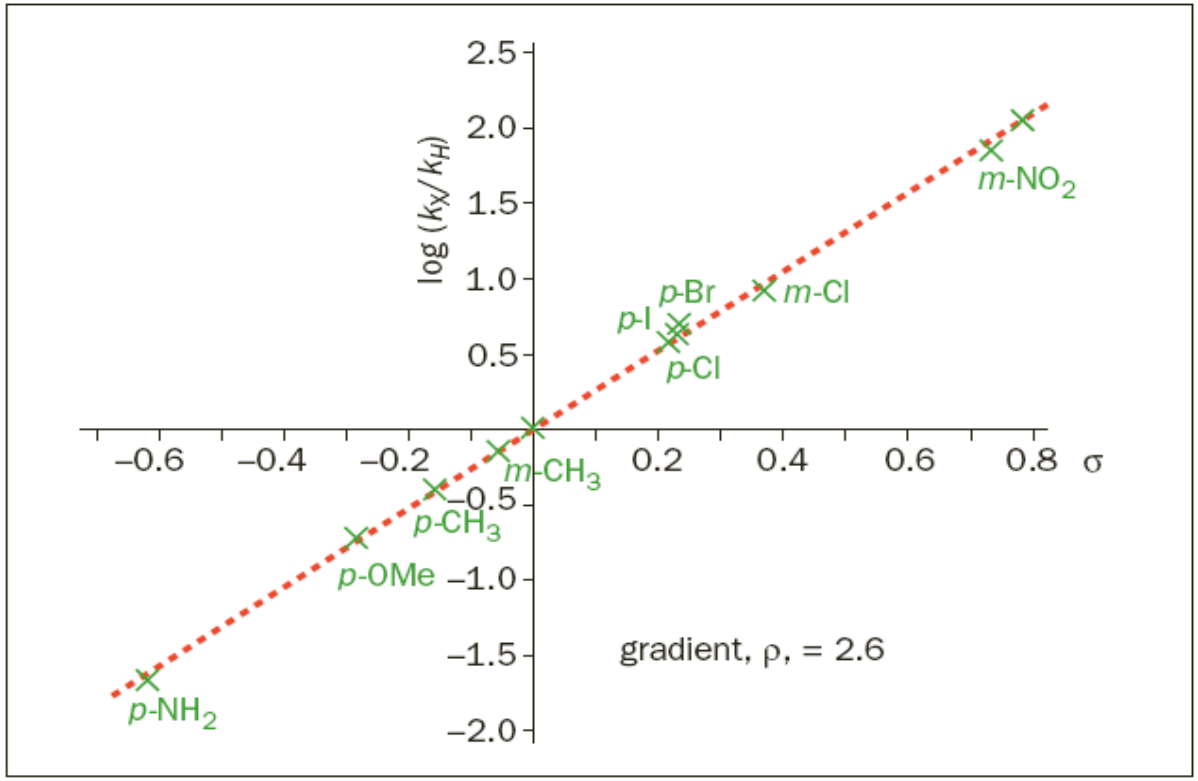
conjugation into ring
not carbonyl group
balances weak effect
of electronegative N:
zero σ_m

σ – **szubsztiuens paraméter(konstans)**

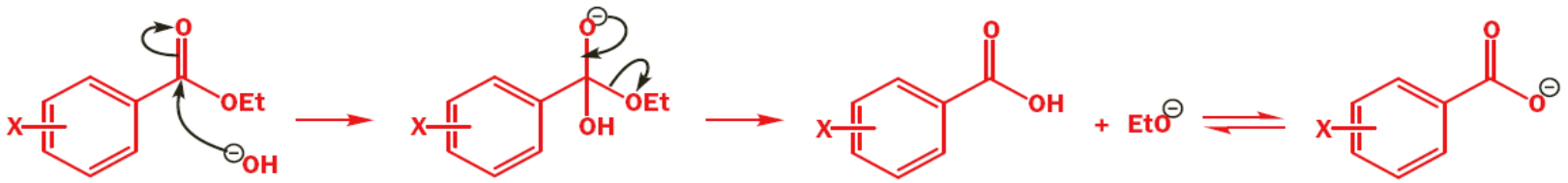
reaction to be investigated

meta- and
para-X only



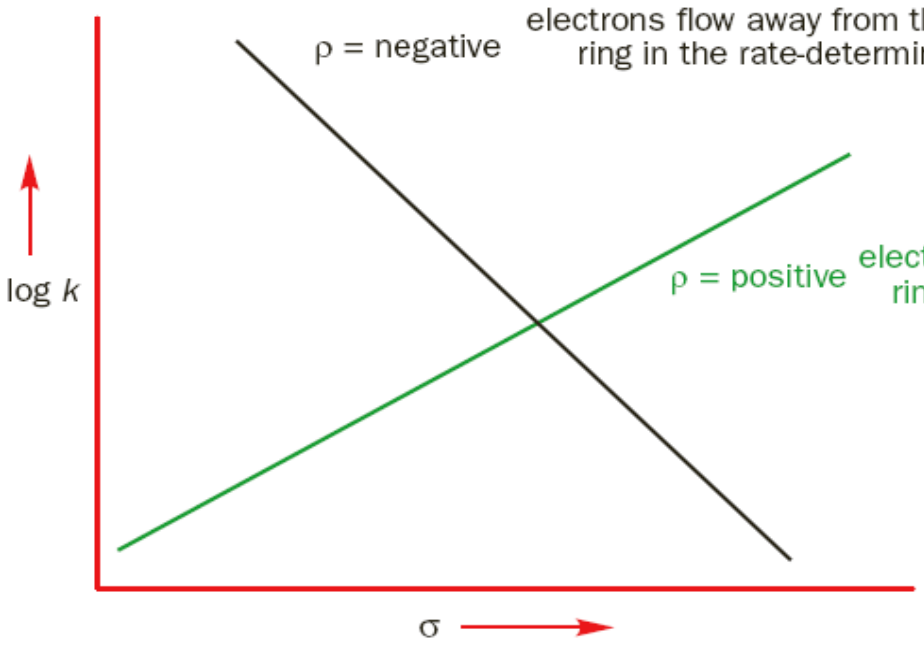

2.5
2.0
1.5
1.0
0.5
–0.5
–1.0
–1.5
–2.0
log (k_X/k_H)
–0.6
–0.4
–0.2
0.2
0.4
0.6
0.8
σ
p-NH2
p-OMe
p-CH3
m-CH3
p-I
p-Br
p-Cl
m-Cl
m-NO2
gradient, ρ, = 2.6

ρ – **reakció paraméter(konstans)**

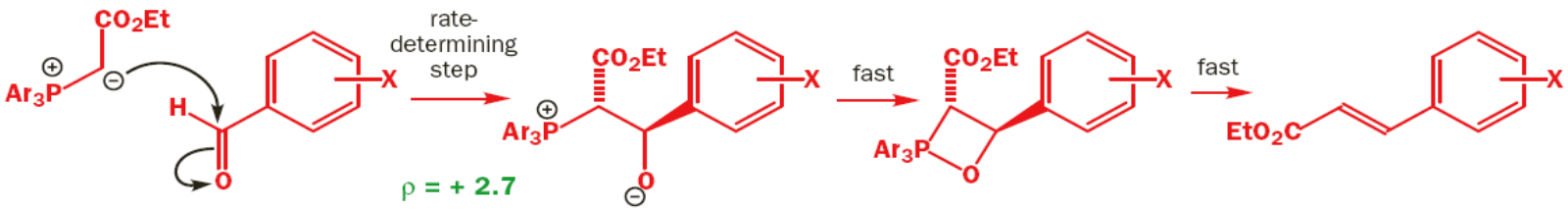

X
O
OEt
OH
X
O
OEt
OH
X
O
OH
+ EtO
X
O
O

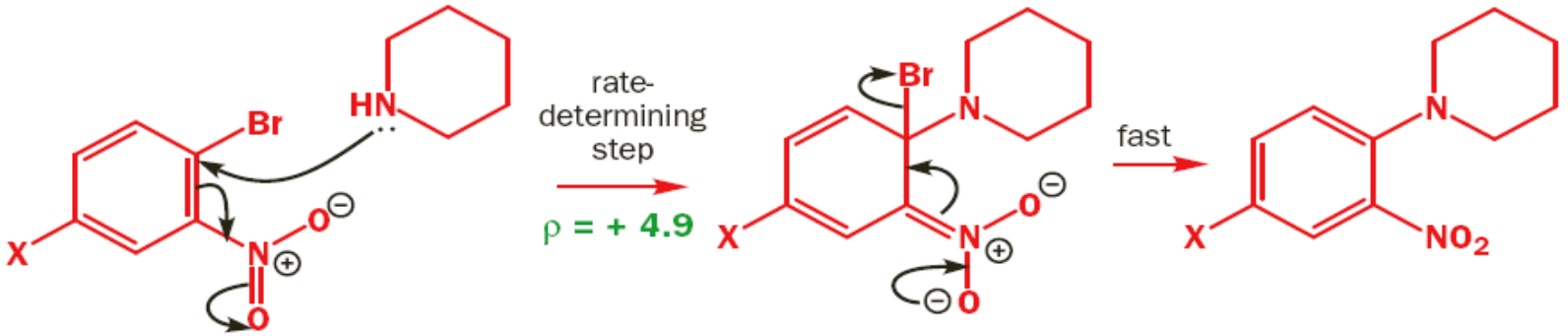
- **The Hammett reaction constant ρ measures the *sensitivity* of the reaction to electronic effects.**
  - A *positive* ρ value means *more* electrons in the transition state than in the starting material
  - A *negative* ρ value means *fewer* electrons in the transition state than in the starting material

typical Hammett plots

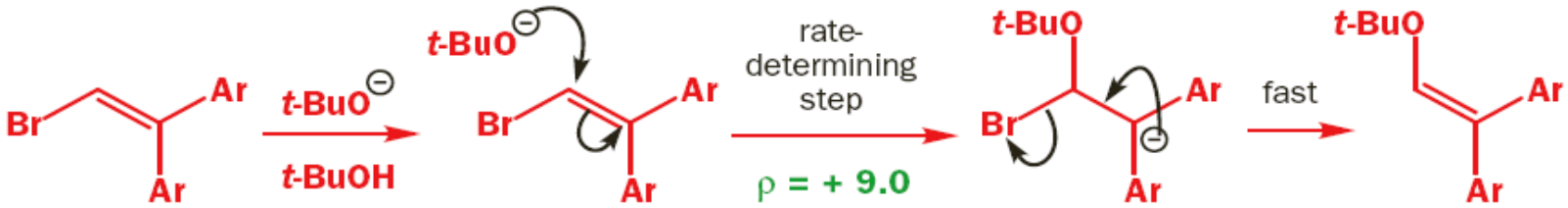


Reakciók pozitív ρ-értékkel

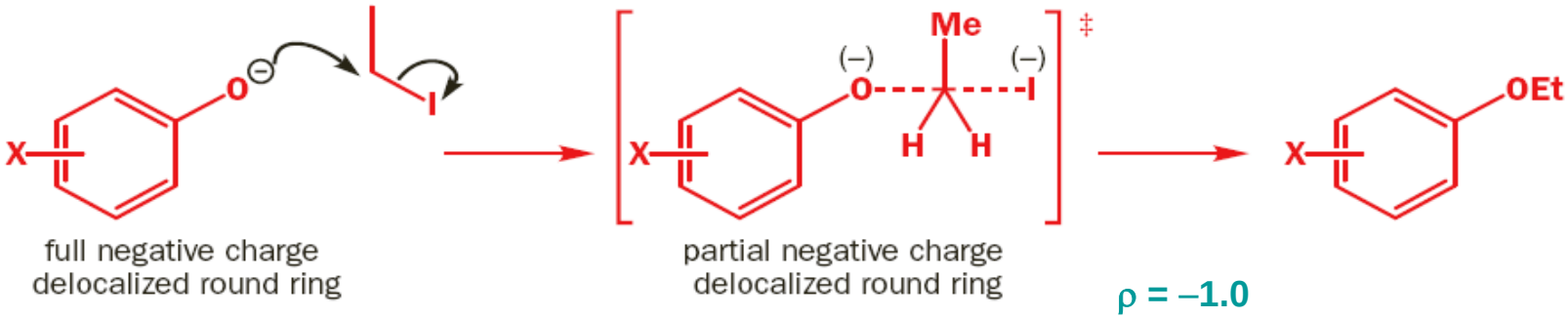


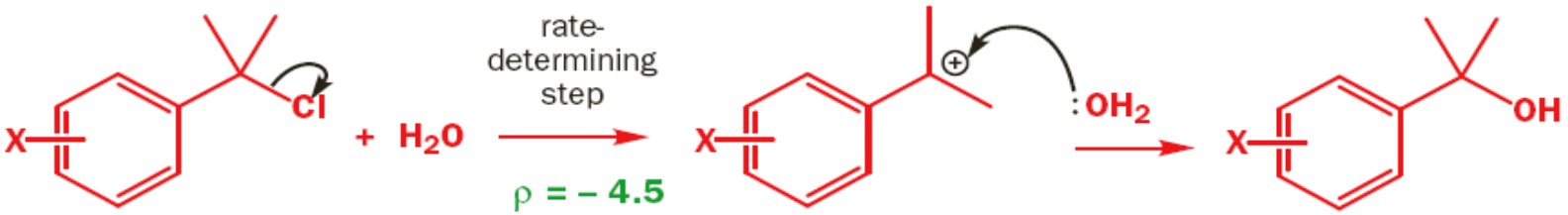


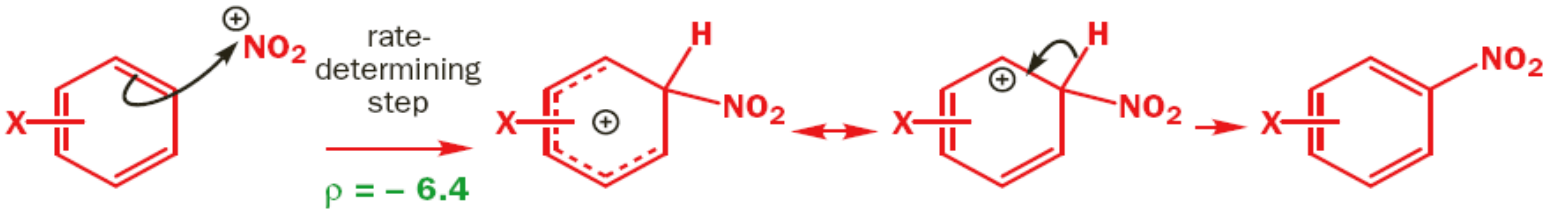
negative charge delocalized round benzene ring



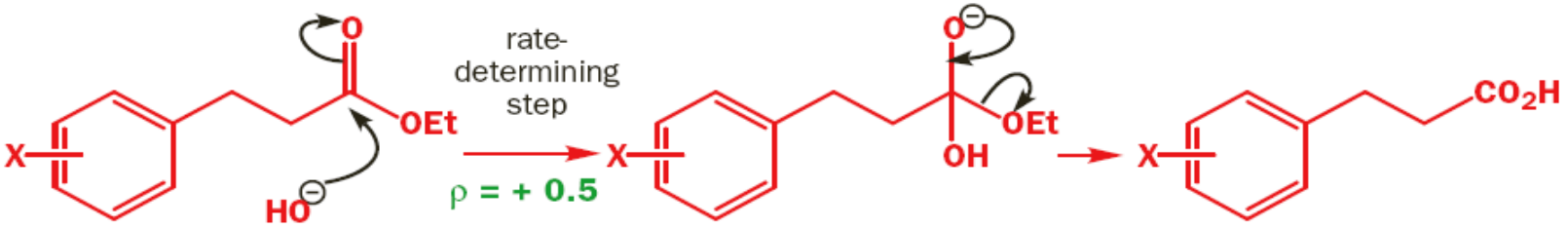
Reakciók negatív ρ-értékkel



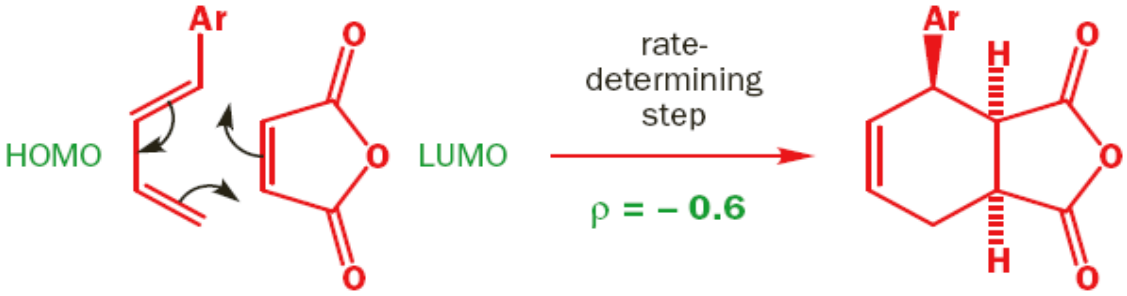




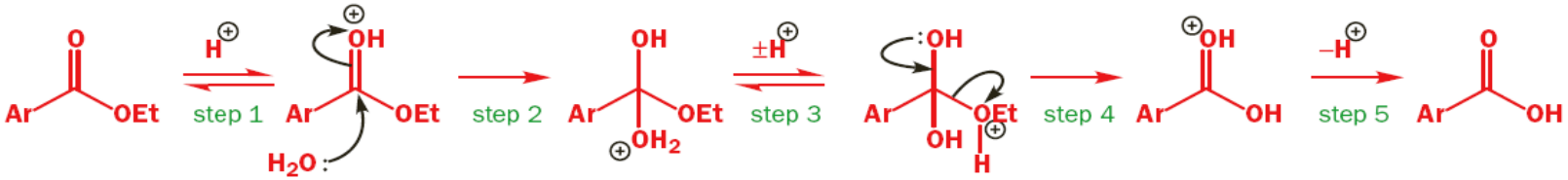
Reakciók kicsi ρ-értékkel



az aromás gyűrű túl messze van a reakciócentrumtól



nem halmozódik fel töltés

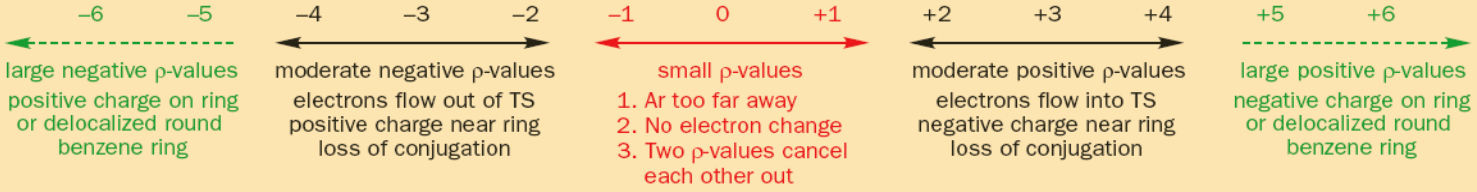


ρ = +0.1

az ρ-értékek kioltják egymást

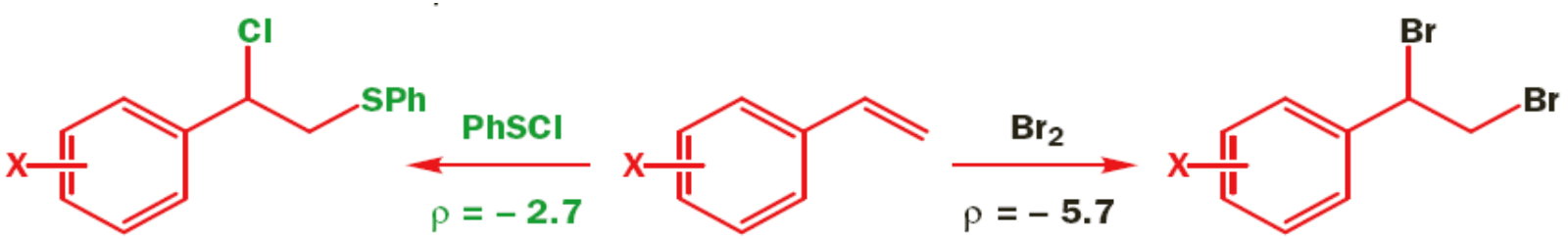
The meaning of Hammett ρ values

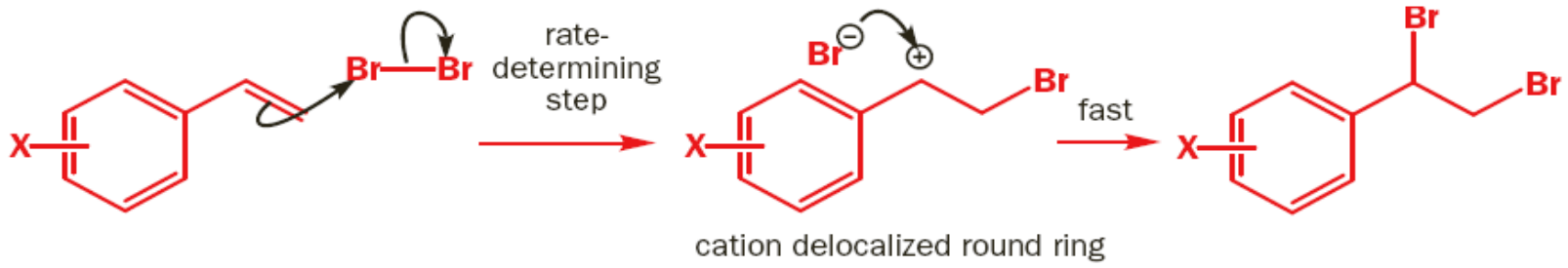
This then is the full picture. You should not, of course, learn these numbers but you need an idea of roughly what each group of values means. You should see now why it is unimportant whether the Hammett correlation gives a good straight line or not. We just want to know whether ρ is + or – and whether it is, say, 3 or 6. It is meaningless to debate the significance of a r value of 3.4 as distinct from one of 3.8.



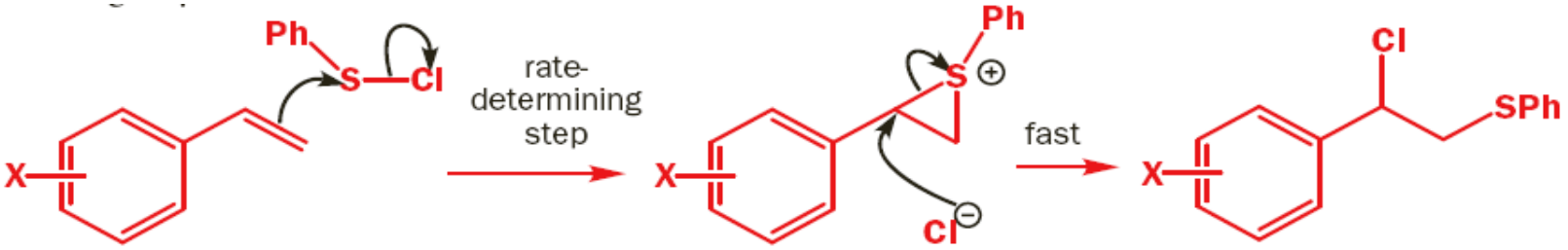
A Hammett-összefüggés felhasználása reakciómechanizmus tanulmányozására

I.

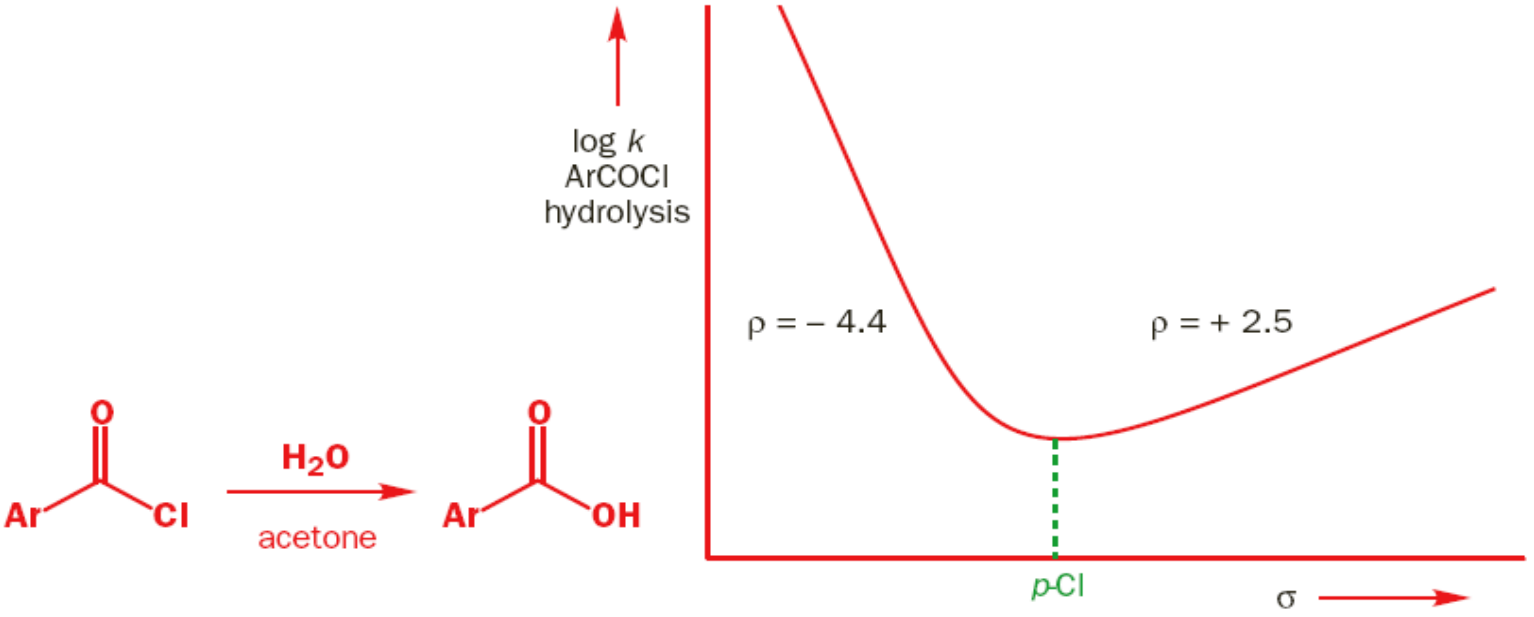


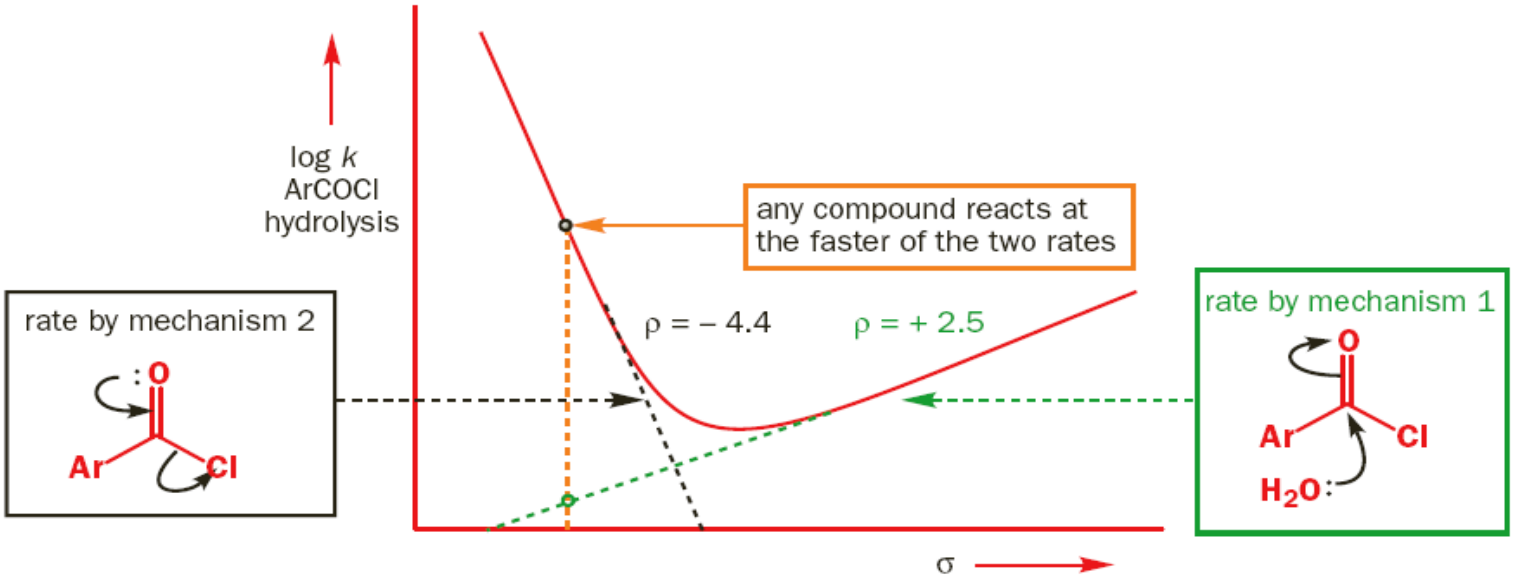


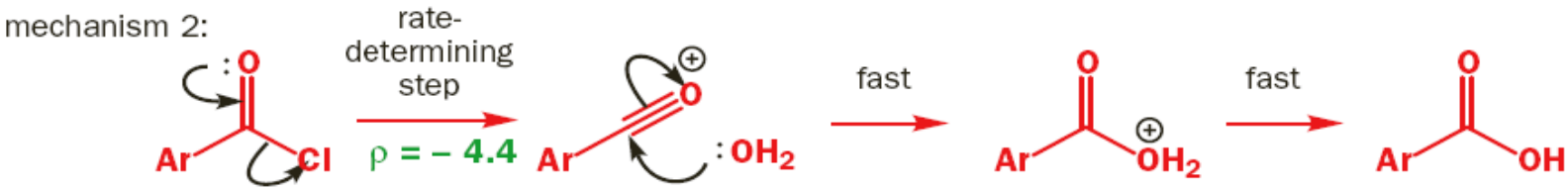
cation delocalized round ring



II.


log k
ArCOCl
hydrolysis
ρ = – 4.4
ρ = + 2.5
p-Cl
σ
O
Ar
Cl
H2O
acetone
O
Ar
OH


log k
ArCOCl
hydrolysis
any compound reacts at
the faster of the two rates
rate by mechanism 2
ρ = – 4.4
ρ = + 2.5
rate by mechanism 1
σ


mechanism 2:
rate-
determining
step
ρ = – 4.4
fast
fast

KÖSZÖNÖM A FIGYELMET!

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