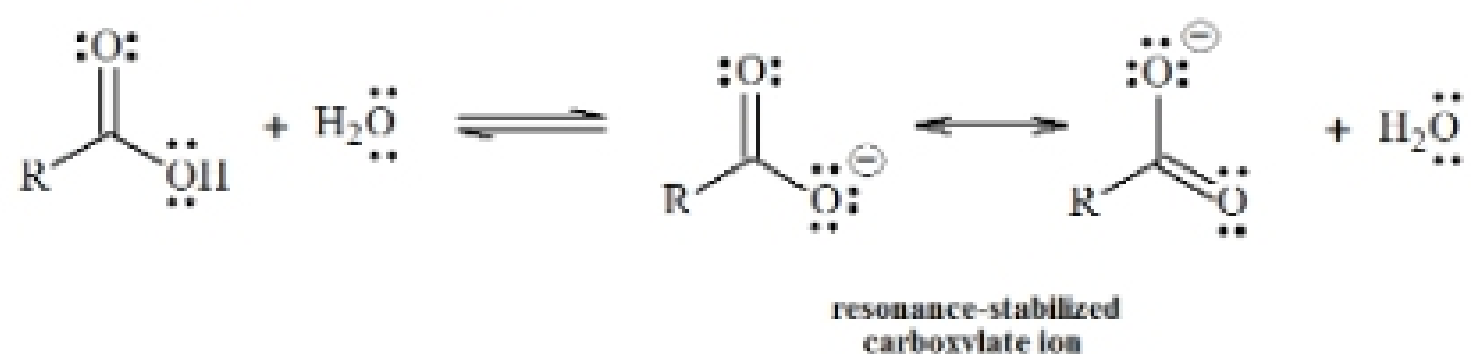


Acidity & Basicity of Carboxylic Acids

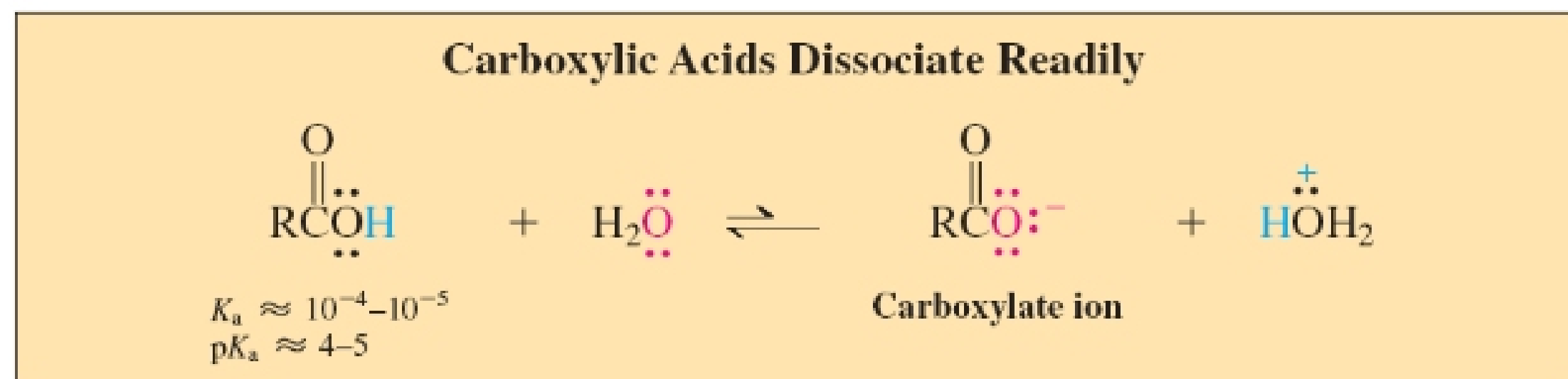
Acidity of Carboxylic Acids



Salt Formation



Carboxylic acids are relatively strong acids.
Carboxylic acids have much lower $\text{p}K_a$ values than do alcohols.

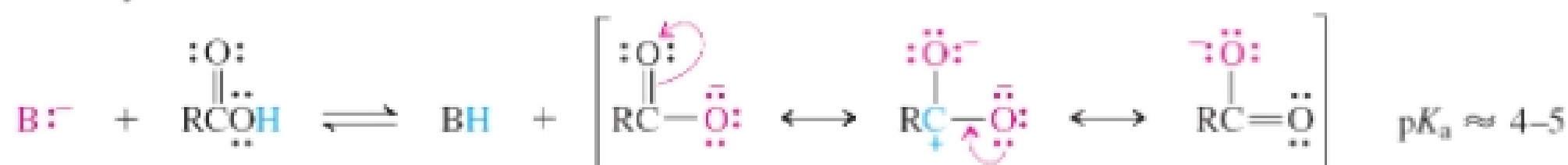


The lowered $\text{p}K_a$ values are due to the electron-withdrawing effect of the positively polarized carbonyl carbon and the resonance stabilization of the carboxylate group.

Resonance in Carboxylate and Enolate Ions

Carboxylate ion

(B = base)



Enolate ion



Two of the three resonance forms of the carboxylate ion are equivalent, leading to a symmetrical ion with equal carbon-oxygen bond lengths (1.26 Å), midway between a carbon-oxygen double bond (1.20 Å) and a carbon-oxygen single bond (1.34 Å).

Electron-withdrawing substituents increase the acidity of carboxylic acids.

The inductive effect of electron-withdrawing groups close to the carboxy group causes an increase in acidity. Three electron-withdrawing groups on the α -carbon sometimes results in acidity near that of some inorganic acids.

TABLE 19-3 pK_a Values of Various Carboxylic and Other Acids			
Compound	pK_a	Compound	pK_a
Alkanoic acids		Dioic acids	
HCOOH	3.55	HOOC-COOH	1.27, 4.19
CH ₃ COOH	4.76	HOOCCH ₂ COOH	2.83, 5.69
ClCH ₂ COOH	2.82	HOOCCH ₂ CH ₂ COOH	4.20, 5.61
Cl ₂ CHCOOH	1.26	HOOC(CH ₂) ₄ COOH	4.35, 5.41
Cl ₃ CCOOH	0.63		
F ₃ CCOOH	0.23	Other acids	
CH ₃ CH ₂ CH ₂ COOH	4.82	H ₃ PO ₄	-2.15 (first pK_a)
CH ₃ CH ₂ CH(Cl)COOH	2.84	HNO ₃	-1.4
CH ₃ CH(Cl)CH ₂ COOH	4.06	H ₂ SO ₄	-3.0 (first pK_a)
ClCH ₂ CH ₂ CH ₂ COOH	4.52	HCl	-8.0
Benzoic acids		H ₂ O	15.7
4-CH ₃ C ₆ H ₄ COOH	4.36	CH ₃ OH	15.5
C ₆ H ₅ COOH	4.20		
4-ClC ₆ H ₄ COOH	3.98		

The dioic acids have two pK_a values.

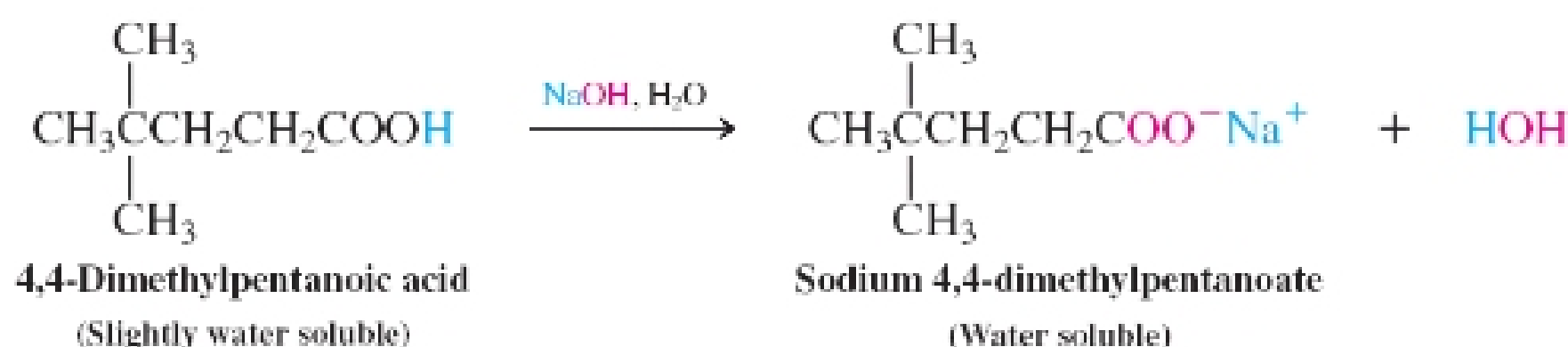
In ethanedioic and propanedioic acids, the first pK_a is lowered by the electron-withdrawing effect of the second.

In higher dioic acids, both pK_a values are close to monocarboxylic acids.

Carboxylate salts of carboxylic acids can be prepared by treatment of the acid with a base, such as NaOH, Na₂CO₃ or NaHCO₃. These salts are much more water soluble than the corresponding acids.

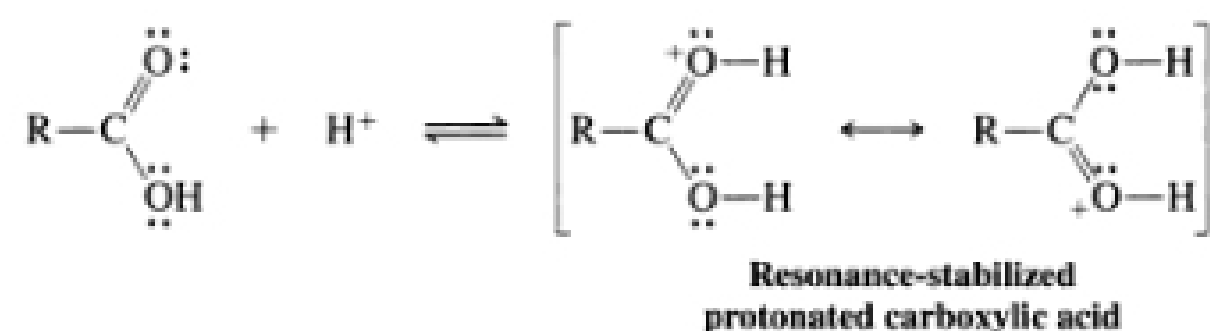
Carboxylate salts are named by specifying the metal and then replacing "ic acid" with "ate".

Carboxylate Salt Formation



Acidity & Basicity of Carboxylic Acids

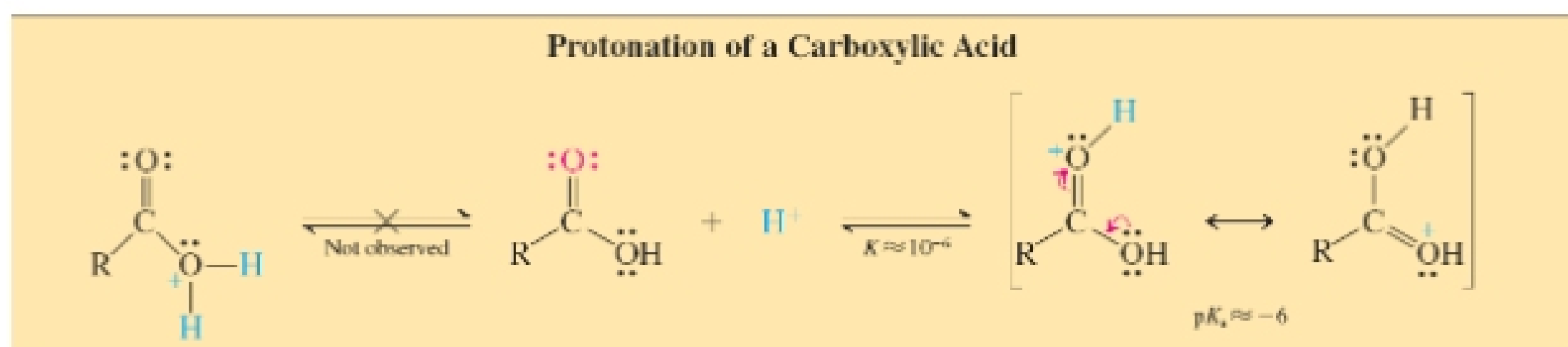
Basicity of Carboxylic Acids



Carboxylic acids may be protonated on the carbonyl oxygen.

The carbonyl oxygen of a carboxylic acid may be protonated by strong acids to give alkyloxonium ions.

The carbonyl oxygen is more basic than the –OH group of alcohols due to resonance stabilization of the alkyloxonium ion.



Note the protonation reaction is not particularly strong.