

9. 電子効果と酸・塩基の強さ Acid-Base Strength and Electronic Effects

重要! 酸-塩基関係は化学平衡である。したがって、速度論 (Kinetics) ではなく熱力学 (Thermodynamics) に基づく取り扱いが必要である。

(復習) 酸解離定数とGibbsエネルギー差 Gibbs Energy Difference

G : Gibbs エネルギー $\Delta G = -RT \ln K_a$

酸解離定数 Acid Dissociation Constant

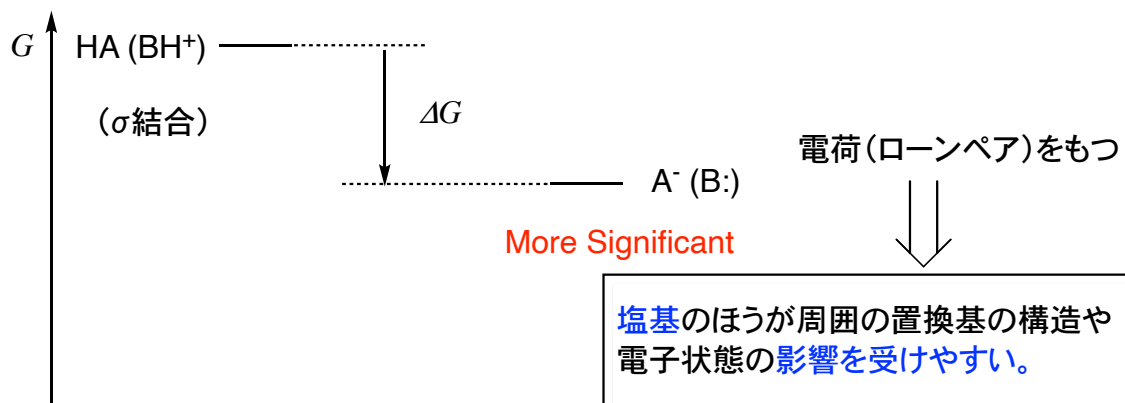
すなわち

$$K_a = \exp\left(-\frac{\Delta G}{RT}\right)$$

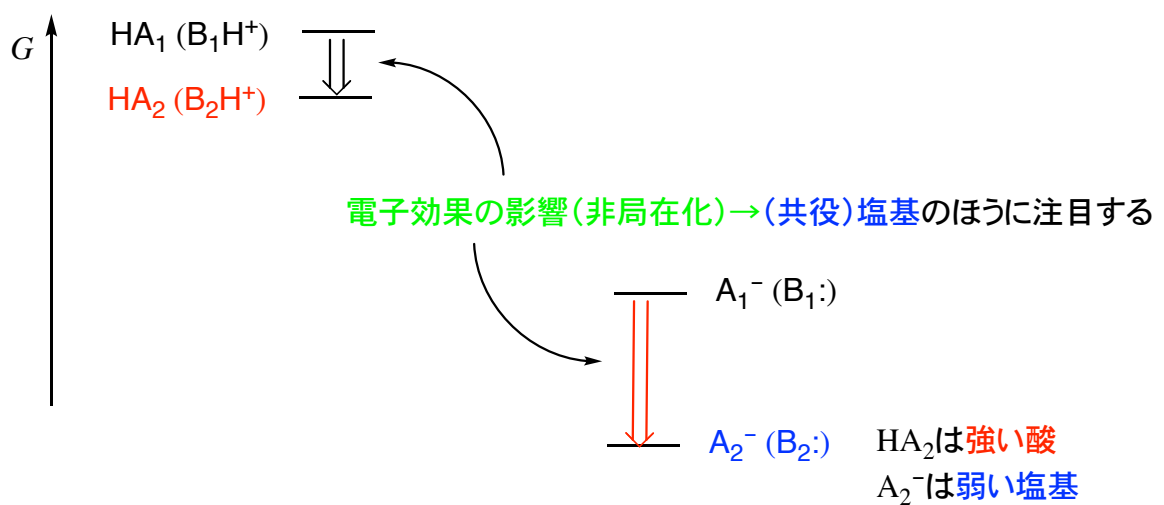
$$K_a = \frac{[\text{SH}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad K_a = \frac{[\text{SH}^+][\text{B}]}{[\text{BH}^+]}$$

強い酸ほどその共役塩基の塩基性は弱い。
強い塩基ほどその共役酸の酸性は弱い。

9.1. 酸と塩基のGibbsエネルギーへの構造の影響



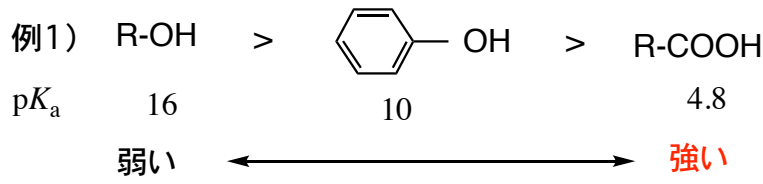
電子効果の異なる2つの酸(塩基)を比較する。



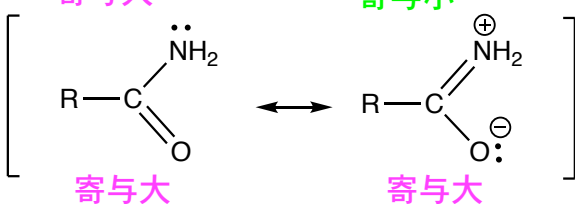
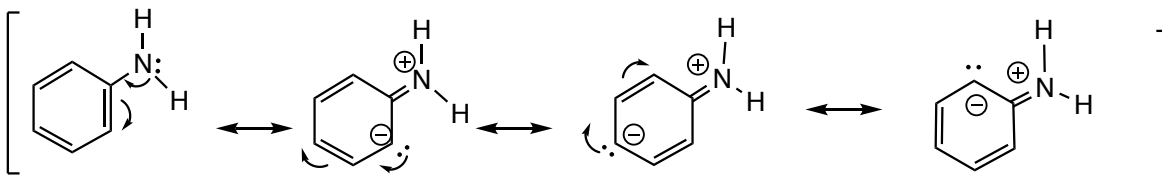
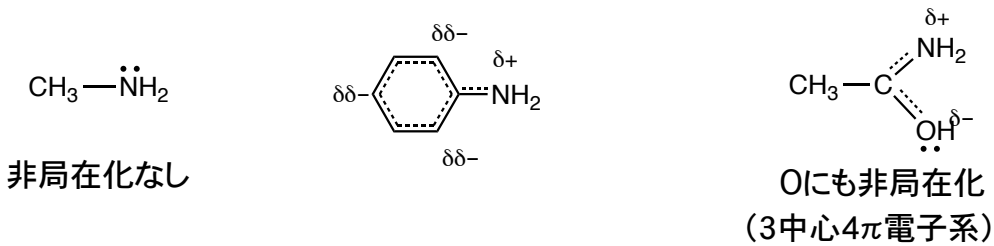
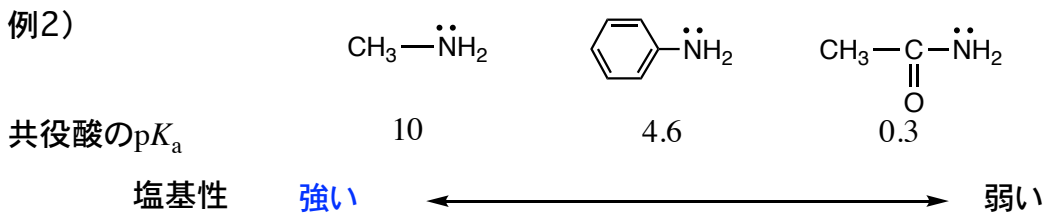
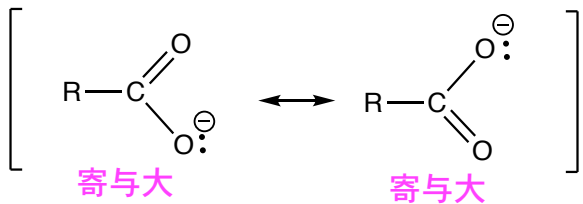
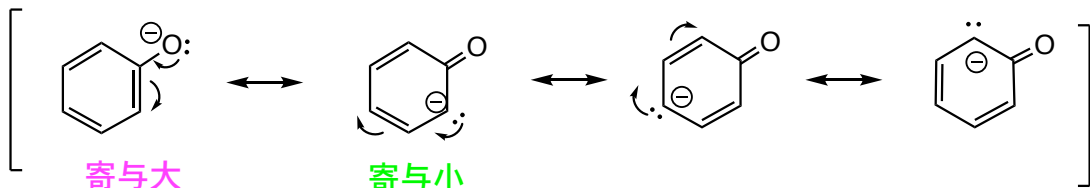
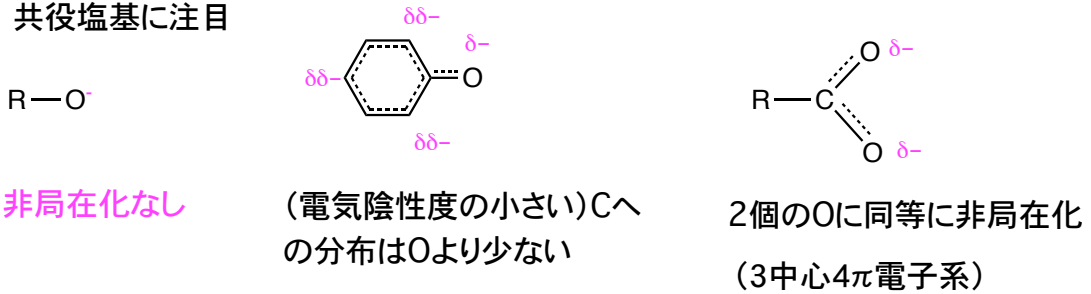
復習:

共役塩基が安定 \implies 強い酸(弱い塩基)

9.2. (復習)官能基の種類と酸(塩基)の強さ Class of Functional Groups



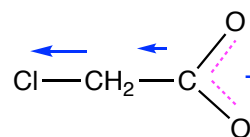
共役塩基に注目



9.3. 電子効果と酸(塩基)の強さ Electronic Effect

1) 誘起効果 Inductive Effect

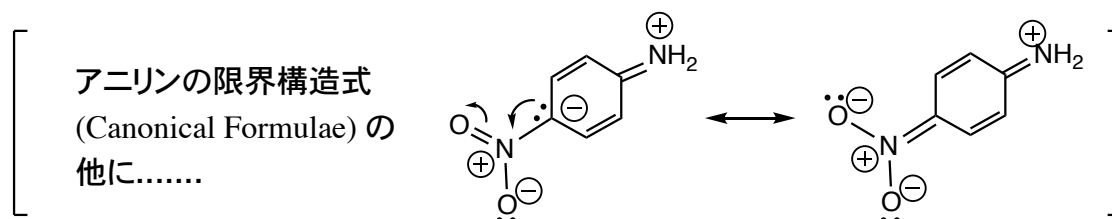
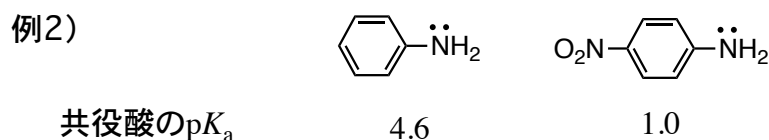
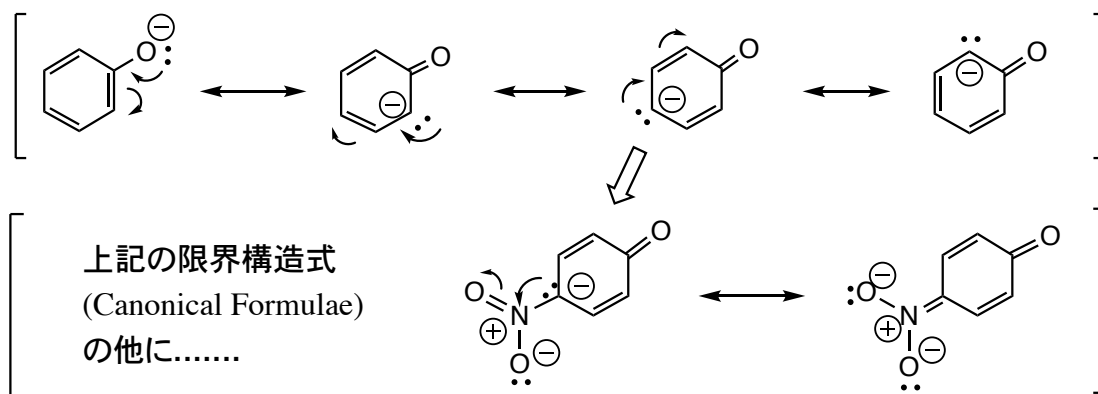
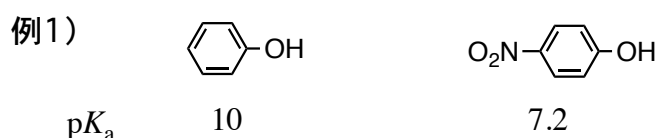
| 例) | | pK_a |
|----|---|--------|
| | CH_3COOH | 4.8 |
| | ClCH_2COOH | 2.8 |
| | $\text{ClCH}_2\text{CH}_2\text{COOH}$ | 4.1 |
| | $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ | 4.5 |
| | $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ | 4.7 |
| | Cl_2CHCOOH | 1.3 |
| | Cl_3CCOOH | 0.7 |
| | FCH_2COOH | 2.6 |



陰性基の誘起効果による負電荷の非局在化

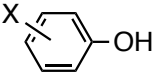
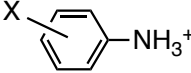
Delocalization of Negative Charge by Inductive Effect

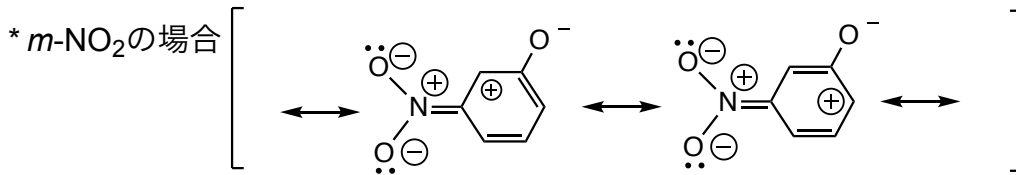
2) 非局在化効果 Delocalization Effect



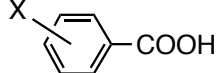
(共役)塩基の電子対の非局在化大→塩基が安定(塩基性弱い)=(共役)酸の酸性強い

例3) 置換 Phenols, Anilines, および安息香酸類 (Benzoic Acids) の pKa

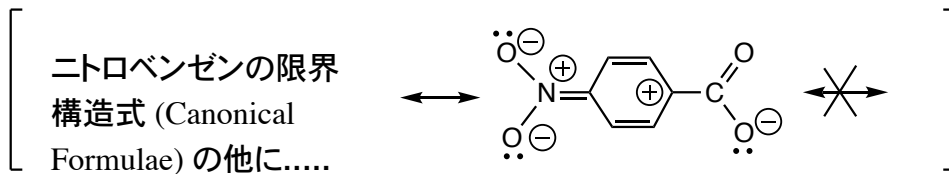
| X |  |  | |
|---------------------------|---|---|------------------|
| H | 10 | 4.6 | |
| <i>m</i> -NO ₂ | 9.3 | 2.6 | 陰性基による誘起効果のみ* |
| <i>p</i> -NO ₂ | 7.2 | 1.0 | } 電子求引基による非局在化効果 |
| 2,4-di NO ₂ | 4.0 | -4.5 | |
| 2,4,6-tri NO ₂ | 0.3 | -9.4 | |



塩基の負電荷の非局在化に寄与しない

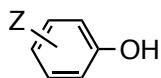
| X |  | |
|---------------------------|---|--------------|
| H | 4.2 | |
| <i>m</i> -NO ₂ | 3.45 | } 陰性基による誘起効果 |
| <i>p</i> -NO ₂ | 3.44 | |

置換基の影響小さい



正電荷は *para* 置換基 (カルボキシ基) までは非局在化しない

例4) 電子供与基 Electron-donating Group が置換したフェノール類



電子供与基 Electron-donating Group は共役塩基の非共有電子対 Unshared Electrons を局在化するため、対応する酸の酸性が弱くなる。

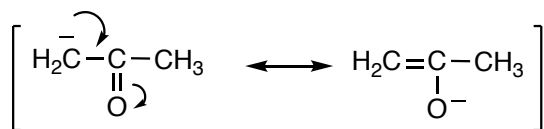
| Z | pK _a |
|---------------------------|-----------------|
| H | 10 |
| <i>p</i> -NH ₂ | 10.3 |
| <i>o</i> -CH ₃ | 10.3 |
| <i>m</i> -CH ₃ | 10.1 |
| <i>p</i> -CH ₃ | 10.3 |

(補足) アルキル基が電子供与基に分類されるのは上の事実が一つの根拠 (π 電子も非共有電子対ももたないが)。実際に電子を供与しているかは微妙。

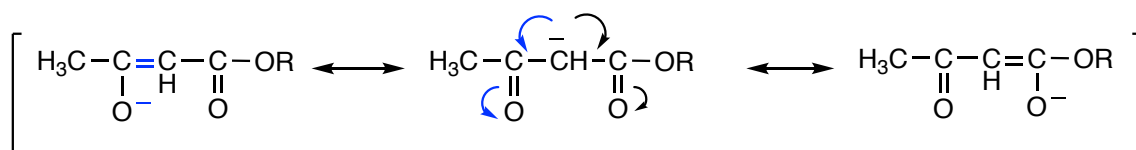
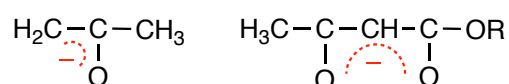
例5) 酸性を示すC-H

| acid | base | pK _a |
|--|--|-----------------|
| CH ₃ COCH ₃ | ⁻ CH ₂ COCH ₃ | 20 |
| CH ₂ (COOR) ₂ | ⁻ CH(COOR) ₂ | 13.5 |
| CH ₃ COCH ₂ COOR | CH ₃ CO ⁻ CHCOOR | 11 |

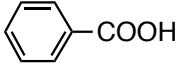
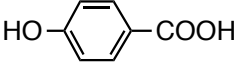
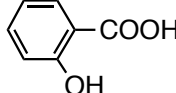
} CH₂: 活性メチレン

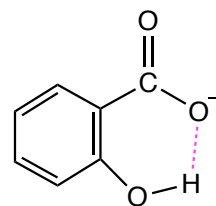


共役塩基の負電荷の非局在化



9.4. (分子内)水素結合と酸(塩基の強さ) (Intramolecular) Hydrogen Bond

| | pK _a |
|---|-----------------|
|  | 4.2 |
|  | 4.6 (+R) |
|  | 2.8 |

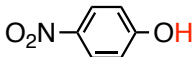
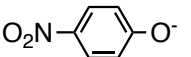
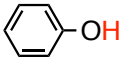
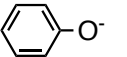
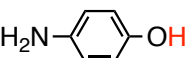
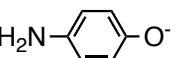
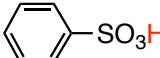
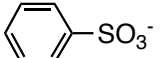
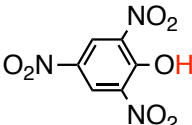
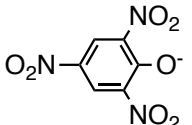
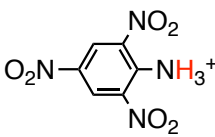
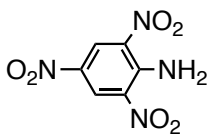
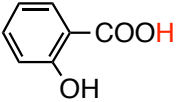
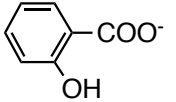
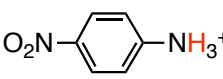
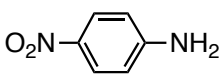
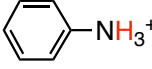
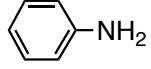
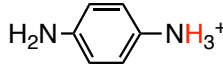
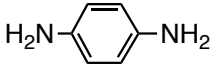
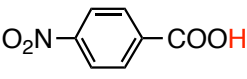
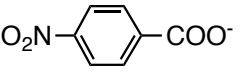
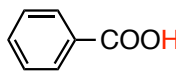
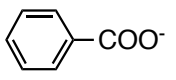


分子内水素結合による負電荷の非局在化

ortho-位の置換基効果は電子効果とは限らない。

まとめ 塩基の非共有電子対 Unshared Electron(負電荷)が非局在化すると、塩基が安定化し、塩基性が弱くなる。すなわち共役酸の酸性が強くなる。

Table. いろいろな化合物のpK_a

| Acid | Base | pK _a | Acid | Base | pK _a |
|---|---|-----------------|--|---|-----------------|
| HI | I ⁻ | -10 | H ₂ CO ₃ | HCO ₃ ⁻ | 6.4 |
| H ₂ SO ₄ | HSO ₄ ⁻ | -10 |  |  | 7.2 |
| HClO ₄ | ClO ₄ ⁻ | -10 | HCN | CN ⁻ | 9 |
| HBr | Br ⁻ | -9 |  |  | 10 |
| HCl | Cl ⁻ | -7 |  |  | 10.3 |
|  |  | -6.5 | CH ₃ COCH ₂ COOR | CH ₃ COCHCOOR | 11 |
| H ₃ O ⁺ | H ₂ O | -1.7 | CH ₂ (COOR) ₂ | ⁻ CH(COOR) ₂ | 13.5 |
| HNO ₃ | NO ₃ ⁻ | -1.5 | H ₂ O | HO ⁻ | 15.7 |
| CF ₃ COOH | CF ₃ COO ⁻ | 0.2 | CH ₃ OH | CH ₃ O ⁻ | 16 |
|  |  | 0.3 | CH ₃ COCH ₃ | CH ₃ COCH ₂ ⁻ | 20 |
| CCl ₃ COOH | CCl ₃ COO ⁻ | 0.7 | H ₃ C-C≡CH | H ₃ C-C≡C ⁻ | 25 |
| H ₂ SO ₃ | HSO ₃ ⁻ | 1.9 | NH ₃ | NH ₂ ⁻ | 36 |
| HSO ₄ ⁻ | SO ₄ ²⁻ | 2.0 | CH ₄ | CH ₃ ⁻ | 49 |
| FCH ₂ COOH | FCH ₂ COO ⁻ | 2.6 |  |  | -9.4 |
|  |  | 2.8 | CH ₃ -C(=O)-NH ₃ ⁺ | CH ₃ -C(=O)-NH ₂ | 0.3 |
| ClCH ₂ COOH | ClCH ₂ COO ⁻ | 2.8 |  |  | 1.0 |
| HF | F ⁻ | 3.2 |  |  | 4.6 |
| HNO ₂ | NO ₂ ⁻ | 3.3 |  |  | 6.1 |
|  |  | 3.4 | NH ₄ ⁺ | NH ₃ | 9.2 |
|  |  | 4.2 | CH ₃ NH ₃ ⁺ | CH ₃ NH ₂ | 10 |
| CH ₃ COOH | CH ₃ COO ⁻ | 4.8 | | | |

注意:pK_aの値は用いた溶媒により大きく異なり、その補正方法にもいくつか報告がある。また、同じ溶媒中でも複数の異なる値が報告されているので、文献によっては上と異なる値が記載されているものもある。値を覚えるのではなく、全体の傾向をつかむことが重要である。