

Chapter 3 Acidity/Basicity and Structure

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Problems

Answers

In the last chapter, we learned that organic compounds are composed of substituents and hydrocarbon moieties. Substituents are also called functional groups to indicate that these govern the physical and chemical properties (*i.e.*, functionality) of the compound in question. If we can estimate the extent and the way of the effect of substituents on the property of organic compounds quantitatively, we will be able to predict the property of an organic compound.

Good examples of quantitative estimation can be found, not in hydrocarbons, but in such compounds as carboxylic acids, phenols and amines, which exhibit acidic or basic properties. The relation between the structure and property of these compounds is of prime importance. Furthermore, measurements of the change of acidity/basicity of an organic compound caused by introducing a substituent is also very important. In this chapter, you will learn the change of acidity/basicity of an organic compound caused by introducing a substituent, so called the **substituent effect**.

3.1 Brønsted-Lowry theory

Among organic compounds, such compounds as carboxylic acids and phenols exhibit acidity and such compounds as amines show basicity. Their acidity/basicity is changed in accordance with the change in structure. This all depends on the substituents that the molecules have. In this regard, the study of acidity/basicity of organic compounds will give you a good opportunity to survey what you have learned so far.

It must be added that the reactivity of organic compounds is deeply related to their acidity/basicity. In this chapter, the acidity/basicity will be discussed not only for acidic and basic compounds, but also for organic compounds in general.

(a) Acid dissociation constant and acid dissociation exponent

Brønsted and Lowry defined an acid as a compound that tends to release H^+ (proton) and a base, as a compound that tends to accept proton in an aqueous solution. For an acid, the easiness of proton release is defined by an **acid dissociation constant** K_a . For dissociation equilibrium of an acid HA,

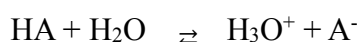


K_a and **acid dissociation exponent** pK_a is defined by the following equations.

$$K_a = \frac{[H^+][A^-]}{[HA]}, \quad pK_a = -\log K_a \quad (3.1)$$

where $[HA]$, $[H^+]$, and $[A^-]$ are the concentration of HA, H^+ and A^- , respectively, at equilibrium.

If we assume that proton does not exist as such in the dissociation equilibrium of an acid, but exists as a hydronium ion H_3O^+ , the dissociation equilibrium is expressed as:



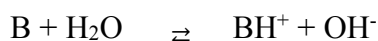
and the corresponding acid dissociation constant K_a' and acid dissociation exponent pK_a'' are defined as below.

$$K_a' = \frac{[H_3O^+][A^-]}{[HA][H_2O]}, \quad pK_a' = -\log K_a' \quad (3.2)$$

Since $[H_2O]$ is almost constant before and after equilibrium, this term can be included in an constant term, K_a . Thus,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}, \quad pK_a = -\log K_a \quad (3.3)$$

For the dissociation equilibrium of Base B;



the base dissociation constant K_b' and base dissociation exponent pK_b' are defined as shown below.

$$K_b' = \frac{[BH^+][OH^-]}{[B][H_2O]}, \quad pK_b' = -\log K_b' \quad (3.4)$$

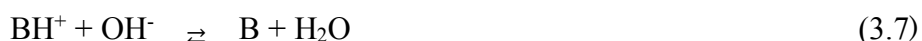
Since $[H_2O]$ is almost constant before and after equilibrium, this term can be included in K_b . Thus,

$$K_b = \frac{[BH^+][OH^-]}{[B]}, \quad pK_b = -\log K_b \quad (3.5)$$

The larger K_a and K_b , the stronger the acid and the base. Accordingly, the smaller pK_a and pK_b , the stronger the acid and the base. Hence, the smaller K_a and K_b , the weaker the acid and the base. Accordingly, the larger pK_a and pK_b , the weaker the acid and the base. For example, at 25°C, K_a and pK_a of acetic acid are 1.75×10^{-5} and 4.86, respectively, and those of phenol are 1.55×10^{-10} and 9.82, respectively. Acetic acid is stronger as an acid than phenol.

(b) Conjugate acid and conjugate base

The chemical entity A^- , obtained from an acid HA by removing H^+ , is called the **conjugate base** of HA . The chemical entity BH^+ , obtained by adding H^+ to a base B , is called the **conjugate acid** of B . A conjugate base of a weak acid is a strong base, and a conjugate acid of weak base is a strong acid. For instance, equilibrium of an acid A weaker than H_2O , and that of a base weaker than H_2O are both shifted to the right side.



Since the strength of a base can be expressed in terms of the acidity of its conjugate acid, two scales, the strength of acids and that of bases, are not necessary. One scale, the strength of acid, will be enough for both acids and bases. The acid dissociation constant of a conjugate acid BH^+ is defined as below.

$$K_a = \frac{[B][H_3O^+]}{[BH^+]} \quad (3.8)$$

By combining Eq. (3.5) and Eq (3.8), the following equation is obtained.

$$K_a K_b = [H_3O^+][OH^-] \quad (3.9)$$

The right side of the equation is the ionic product of H₂O, $K_w = 1.0 \times 10^{-14}$ (25 °C). Eq. (3.9) is now as below.

$$K_a K_b = K_w \quad (3.10)$$

This can be converted to dissociation exponent shown below.

$$pK_a + pK_b = 14 \quad (3.11)$$

Since pK_b of ammonia is 4.76, pK_a of ammonium ion, the conjugate acid of ammonia, is

$$14 - 4.76 = 9.24.$$

As is clear from the fact that the ionic product of water is employed, the strength of acids HA and BH⁺ are determined by comparing that of H₂O. Then there will arise a question whether we can apply this method to organic compounds, which in many cases are hardly soluble in water.

In principle, such a comparison is possible, and the strength of all acids and conjugate acids (of bases) with one standard, pK_a .

Point: Dissociation constants of acids and bases

For HA, an acid:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}, \quad pK_a = -\log K_a$$

For B, a base:

$$K_b = \frac{[BH^+][OH^-]}{[B]}, \quad pK_b = -\log K_b$$

For BH⁺, a conjugate acid of B,

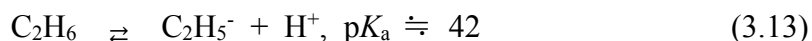
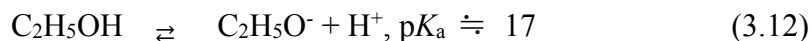
$$K_a = \frac{[B][H_3O^+]}{[BH^+]}$$

Where

$$pK_a + pK_b = 14$$

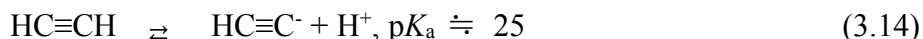
(c) Extension of the concept of acids and bases

So far you learned that such compounds as carboxylic acids and phenols are acidic organic compounds. In order to study the reactivity of organic compounds thoroughly, you must include much wider range of organic compounds as acids, starting from alcohols that bear some hydrogen atom(s) that relatively easily dissociate as proton(s) to such compounds as hydrocarbons which you have never thought these are acidic. This means you have to handle such equilibriums as shown below.



Indeed, the dissociation constant of ethane is very small (the dissociation exponent is very large). In terms of the number of dissociated molecule, one out of about 10^{21} molecules dissociates. Dissociation exponent of ethanol is close to that of water.

Though acetylene is a hydrocarbon, its dissociation exponent is fairly small as compared with that of ethane.

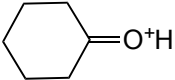
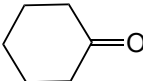


This value, much smaller than that of ethane, corresponds to the higher reactivity of acetylene. It readily forms such a metal acetylide as $\text{HC}\equiv\text{CAg}$. This reaction is related to the high acidity of acetylenic proton.



In Table 3.1, $\text{p}K_{\text{a}}$ values of a variety of organic compounds are summarized. This table will be the key to understand the relation between the structure and reactivity of organic compounds. For instance, this table is indispensable to understand the Aldol condensation (Ch. 11) or malonic ester synthesis (Ch. 12).

Table 3.1 pK_a values of a variety of organic compounds

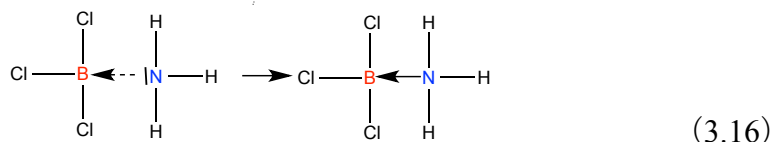
conjugate acid	pK_a	conjugate base
ethane CH_3CH_3	42	CH_3CH_2^-
methane CH_4	40	CH_3^-
benzene C_6H_6	37	C_6H_5^-
ethylene $\text{CH}_2=\text{CH}_2$	36	$\text{CH}_2=\text{CH}^-$
ammonia NH_3	36	NH_2^-
propene $\text{CH}_2=\text{CHCH}_3$	35	$\text{CH}_2=\text{CHCH}_2^-$
aniline $\text{C}_6\text{H}_5\text{NH}_2$	25	$\text{C}_6\text{H}_5\text{NH}^-$
acetylene $\text{CH}\equiv\text{CH}$	25	$\text{CH}\equiv\text{C}^-$
acetone CH_3COCH_3	20	$\text{CH}_3\text{COCH}_2^-$
<i>t</i> -butylalcohol $(\text{CH}_3)_3\text{COH}$	~ 19	$(\text{CH}_3)_3\text{CO}^-$
alcohols ROH	~ 17	RO^-
amides RCONH_2	~ 16	RCONH^-
water H_2O	15.7	OH^-
malonic ester $\text{CH}_2(\text{COOR})_2$	13.5	$(\text{ROOC})_2\text{CH}^-$
RNH_3^+ , R_2NH_2^+ , R_3NH^+	~ 10	amines RNH_2 , R_2NH , R_3N
nitromethane CH_3NO_2	10.2	O_2NCH_2^-
phenol $\text{C}_6\text{H}_5\text{OH}$	10	$\text{C}_6\text{H}_5\text{O}^-$
NH_4^+	9.2	ammonia NH_3
acetylacetone $\text{CH}_3\text{COCH}_2\text{COCH}_3$	9.0	$\text{CH}_3\text{COCH}=\text{C}(\text{O}^-)\text{CH}_3$
carbonic acid H_2CO_3	6.5	HCO_3^-
$\text{C}_6\text{H}_5\text{NH}_3^+$	4.6	aniline $\text{C}_6\text{H}_5\text{NH}_2$
carboxylic acids RCOOH	4.5 ± 0.5	RCOO^-
$\text{CH}_3\text{CONH}_3^+$	0.3	acetamide CH_3CONH_2
trifluoroacetic acid CF_3COOH	0	CF_3COO^-
nitric acid HNO_3	-1.4	NO_3^-
CH_3OH_2^+	-2	methanol CH_3OH
$\text{H}_3\text{C}-\overset{\text{O}^+\text{H}}{\underset{\text{OH}(\text{R})}{\text{C}}}$	-6.2	acetic acid or R acetate $\text{CH}_3\text{COOH}(\text{R})$
	-6.8	 cyclohexanone
$\text{C}_6\text{H}_5\text{CH}=\text{OH}^+$	-7.1	benzaldehyde $\text{C}_6\text{H}_5\text{CHO}$
$\text{RC}\equiv\text{NH}^+$	~ -10	nitriles $\text{RC}\equiv\text{N}$
$\text{R}-\overset{\text{OH}}{\underset{\text{O}}{\text{N}^+}}$	~ -11	nitro compound RNO_2
perchloric acid HClO_4	~ -20	ClO_4^-
$\text{SbF}_4 \cdot \text{FSO}_3\text{H}$ (superacid)	< -20	$\text{SbF}_4 \cdot \text{FSO}_3^-$

3.2 Lewis's theory

(a) Outline of Lewis's theory

The theory of Brønsted and Lowry emphasized the role of proton in acid-base reactions. The theory proposed by G. N. Lewis (1875-1946) features the role of lone pairs in acid-base reactions. According to Lewis's theory, an acid is defined as a substance that can accept an electron pair, and a base as a substance that can donate an electron pair.

A good example of Lewis's theory is the reaction between boron trichloride BCl_3 and ammonia.



Since boron is a group 13 element, it has only three valence electrons. Hence there are only six electrons around the boron atom of BCl_3 and is electron-deficient. To the contrary, the nitrogen atom of NH_3 has a pair of unshared electrons (lone pair) since it is a group 15 element with five valence electrons.

The lone pair on nitrogen coordinates to the vacant orbital of the boron atom to form a coordination bond. In Lewis's theory, BCl_3 , which accepts a lone pair, is an acid (a **Lewis acid**) and NH_3 , which donates a lone pair, is a base (a **Lewis base**). In other words, this reaction is an acid-base reaction and the product is named as a **Lewis salt**.

Point: Acid-base theory

The Brønsted-Lowry theory

acid \rightarrow proton donor

base \rightarrow proton acceptor

The Lewis theory

acid \rightarrow lone pair acceptor

base \rightarrow lone pair donor

(b) Lewis's theory in organic chemistry

Since such a base as a Lewis base can accept a proton, it is also an acid in the frame of the Brønsted and Lowry theory. However, such a Lewis acid as BCl_3 cannot donate a proton, and is not an acid in the frame of the Brønsted-Lowry theory. Thus, in the frame of Lewis's theory, wider ranges of compounds which do not have protons are acids.

Lewis acids play a very important role in organic reactions. For instance, a typical Lewis acid, aluminum chloride, works as a catalyst in Friedel-Crafts reaction (Ch. 7.3). Table 3.2 gives some Lewis acids frequently used in organic chemistry.

Table 3.2 Representative Lewis acids

name	chemical formula
aluminum chloride	AlCl ₃
iron(III) bromide	FeBr ₃
tin(II) chloride	SnCl ₂
sulfur(III) trioxide	SO ₃
boron trifluoride	BF ₃

Exercise 3.1 Lewis acid

Choose Lewis acids from compounds given below.

Fe(III) chloride FeCl₃

Zinc(II) chloride ZnCl₂

trimethylborane (CH₃)₃B

trimethylamine (CH₃)₃N

ammonium ions NH₄⁺

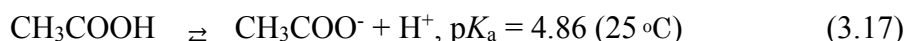
Answer

Fe(III) chloride, Zinc(II) chloride, trimethyl borane.

Trimethylamine is electron-excess and works as a Lewis base. Ammonium ion has no Lewis acidic or basic properties since its outer electron shell is filled.

3.3 Acidity of carboxylic acids**(a) Carboxylic acids and alcohols**

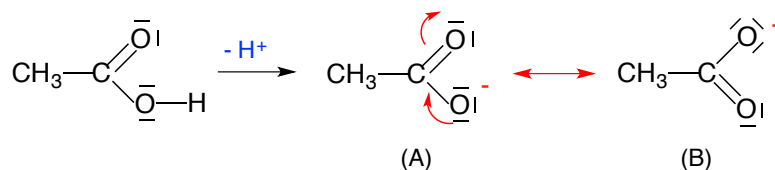
An aqueous solution of a carboxylic acid, acetic acid CH₃COOH as an example, exhibits acidic property because of dissociation equilibrium. Many carboxylic acids are not so much soluble in water, but a similar equilibrium takes place in such organic solvents as ethanol.



The extent of dissociation, as indicated by pK_a values is not necessarily large. pK_a of acetic acid is 4.86. However, this value is considerably large as compared with those of alcohols, *ca.* 17 for ethanol.

The difference of dissociation constant is *ca.* the 12th power of ten, and the dissociation equilibrium of acetic acid is much more shifted to the right as compared with that of ethanol. This difference is explained in terms of resonance.

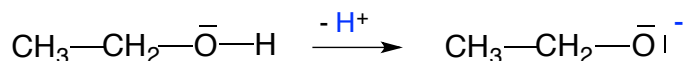
It is possible to write resonance formula (A) and (B) for the carboxylate COO⁻ formed as a result of dissociation. In other words, carboxylate ions are stabilized by resonance.



The small bars – around atoms represent lone pairs. Care should be taken for the change of the

number of bars as a reaction proceeds. Curly arrows with two arrowheads indicate the movement of lone pairs, and curly arrows with one arrowhead indicate movements of unpaired electrons.

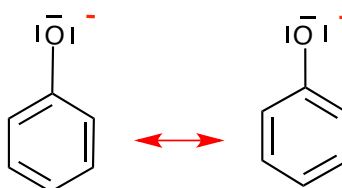
Oxygen atoms bear negative charges in the resonance formula of carboxylate, indicating it can be stable. Two resonance formulas (A) and (B) are comparable to two Kekulé structures of benzene. An ethoxide ion, formed by dissociation of ethanol, does not have such a resonance formula, and consequently has no particular stability.



(b) Carboxylic acids and phenols

The acidity of phenol $\text{C}_6\text{H}_5\text{OH}$ ($\text{p}K_{\text{a}} = 9.82$) is much smaller than that of acetic acid but much larger than that of ethanol. Phenol is less acidic than acetic acid because it lacks a $>\text{C}=\text{O}$ moiety, and more acidic than ethanol because it has a phenyl group. Let us consider the role of a benzene ring in phenols.

It is possible to draw several resonance formulas for a phenoxide ion $\text{C}_6\text{H}_5\text{O}^-$ formed by the dissociation of phenol. First, the resonance formula for benzene ring itself: this will explain at least in part the larger stability of phenoxide ion over ethoxide ion.



The negative charge on the oxygen atom of phenoxide ion can delocalize into the benzene ring, and four resonance formulas can be drawn (Figure 3.1(A)-(D)). For resonance formula (B)-(D), the negative charge delocalizes on the carbon atom and this type of resonance formula is unstable, and these (B)-(D) contribute much less to the stabilization than (A).

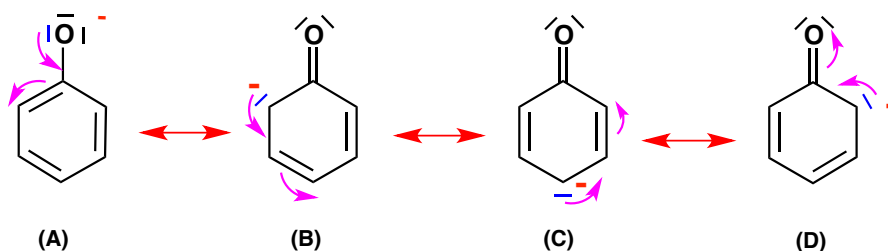


Figure 3.1 Resonance formulas of phenoxide ion; $\text{p}K_{\text{a}} = 0.82$ (25°C)

The two resonance formulas of carboxylate ion are identical and both have the delocalized negative charge on oxygen. In such cases much larger stabilization is expected as compared with the case of phenoxide ion. This is the reason why the acidity of carboxylic acids is larger than that of phenols.

Resonance formulas (B)-(D) indicate that a part of negative charge on the oxygen atom of phenoxide ion delocalizes into the benzene ring. This indicates that O^- has an electron donating effect on the benzene ring, *i.e.*, $-R$ effect.

3.4 Substituent effects

(a) Inductive effect

You have learned in the previous section that the acidity of carboxylic acids is larger than that of phenols and it is due to the presence of carboxylate group. The next step to learn is whether the acidity of carboxylic acids may be influenced by the structure of the rest of the molecule.

Since there is not much difference between pK_a of acetic acid (4.86) in which the carboxylate moiety is bonded to sp^3 hybridized carbon atom and that of benzoic acid (4.20) in which the carboxylate moiety is bonded to sp^2 hybridized carbon atom, the effect of hybridization state of the bonding atom is not very large. If, however, electron-withdrawing substituents having atoms with large electronegativity are introduced into the rest of the molecule, the dissociation is generally enhanced (to make pK_a smaller). It is because the substituent delocalizes the negative charge to the whole molecule, and consequently stabilizes the carboxylate ion.

If hydrogen atoms of methyl group of acetic acid are replaced by chlorine atoms (with large electronegativity) in sequence, pK_a will gradually become smaller because $+I$ effect of chlorine atoms withdraws electron from the bonding carbon (Figure 3.2)

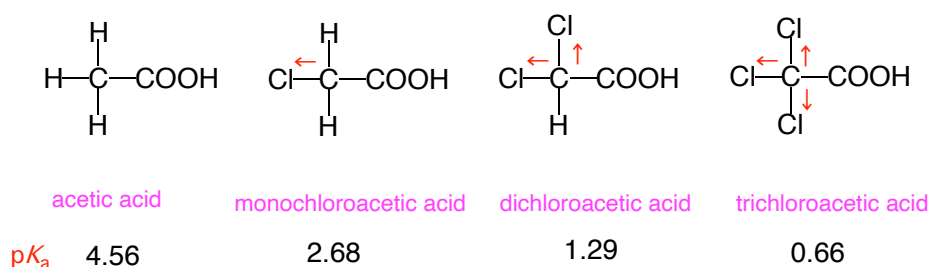


Figure 3.2 $+I$ effect of the substituent

In these cases, all halogen atoms are bonded to α carbon atom (C_α , the bonding atom). As the distance between chlorine atoms and carboxylate moiety will be larger, the substituent effect will rapidly reduce. For instance, 3-chloropropanoic acid in which the chlorine atom is bonded to C_β , the substituent effect is small ($pK_a = 3.92$). Such significant distance dependence is a characteristic of I -effect.

Exercise 3.2 Acidity of acetic acid derivatives

Which of fluoroacetic acid and chloroacetic acid has larger acidity?

Answer

Since the electronegativity of fluorine and chlorine is 4.1 and 2.8, respectively, it is expected that fluoroacetic acid is stronger. In fact, the pK_a values of these two acids are 2.39 and 2.68, respectively. Indeed, fluoroacetic acid is stronger, but the difference is not so large.

(b) Resonance effect caused by substituents

(1) Resonance effect in nitrobenzene

The chlorine atom of chloroacetic acid affects the acidity of carboxylic acid solely by its inductive effect. Some substituents affect the acidity by resonance. A representative substituent of

this kind is a nitro group; as shown below, many resonance formulas can be drawn for nitrobenzene $C_6H_5NO_2$.

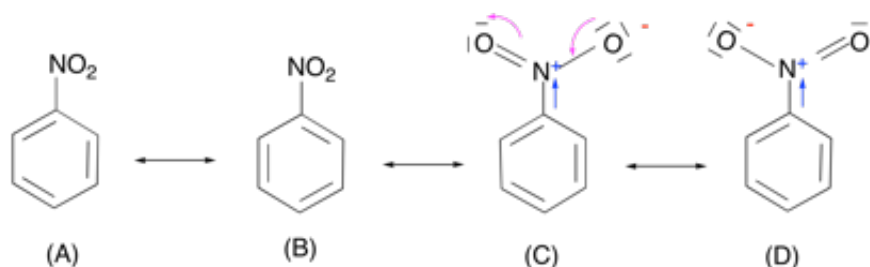


Figure 3.3 Resonance formula of nitrobenzene (1)

Resonance formulas (A) and (B) in Figure. 3.3 are of the benzene ring and has no relation with the nitro group. Resonance formulas (C) and (D) are similar with those of carboxylate ion, and electrons move within the nitro group by resonance. The feature of these resonance formulas is the positive charge on nitrogen atom. Due to this positive charge, a nitro group exhibits a strong electron withdrawing $+I$ effect.

There is another type of resonance formula like (E)-(G) in which the electrons spread over the nitro group and the benzene ring. In these resonance formulas, electrons shift from benzene ring to nitro group, making ortho and para carbon atoms selectively electron deficient. Thus, a nitro group exhibits electron-withdrawing resonance effect, *i.e.*, $+R$ effect. This is contrary to the effect of phenoxide ion which makes ortho and para carbon atoms selectively electron rich, *i.e.*, $-R$ effect.

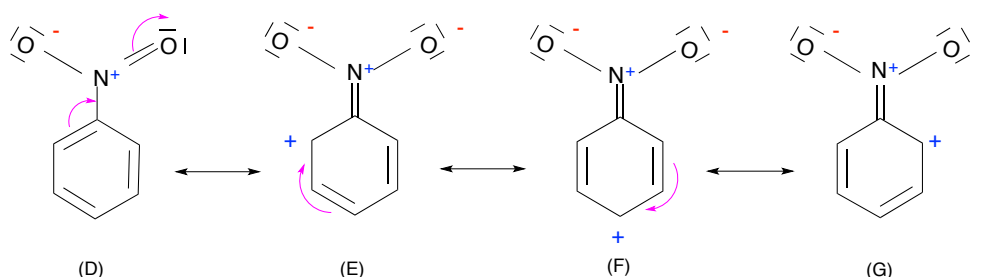


Figure 3.4 Resonance formulas of nitrobenzene (2)

(2) Resonance effect in nitrophenol

In the phenoxide ion, electrons on the oxygen atoms are moved to the benzene ring by resonance. If a nitro group is located at an appropriate position for resonance, electrons on the oxygen atom of phenoxide ion may shift to the nitro group *via* benzene ring. Let us compare the acidity of *p*-nitrophenol with that of phenol.

As for the resonance formulas of *p*-nitrophenoxide ion, there are those due to the resonance of benzene ring, resonance formulas (A) and (B) corresponding to the shift of electron within the nitro group, and resonance formulas (C) and (E) in which electrons remain in the benzene ring. In addition, there is one (D) in which electrons on the oxygen atom of phenoxide ion are moved to the nitro group *via* benzene ring (Figure. 3.5). The phenoxide ion does not have such a resonance formula as (D). Because of the contribution of resonance formula (D), *p*-nitrophenoxide ion is more stable than phenoxide ion. Hence the acidity of *p*-nitrophenol ($pK_a = 7.15$) is higher than that of phenol ($pK_a = 9.82$).

Not only the nitro group, but also many other substituents possessing movable electron pairs

exhibit the resonance effects between the substituent and the reaction center. When both the substituent and the reaction center bind to a benzene ring, these must be either in ortho or para relation so that an effective resonance takes place between the two. No resonance will occur if the two are in meta relation.

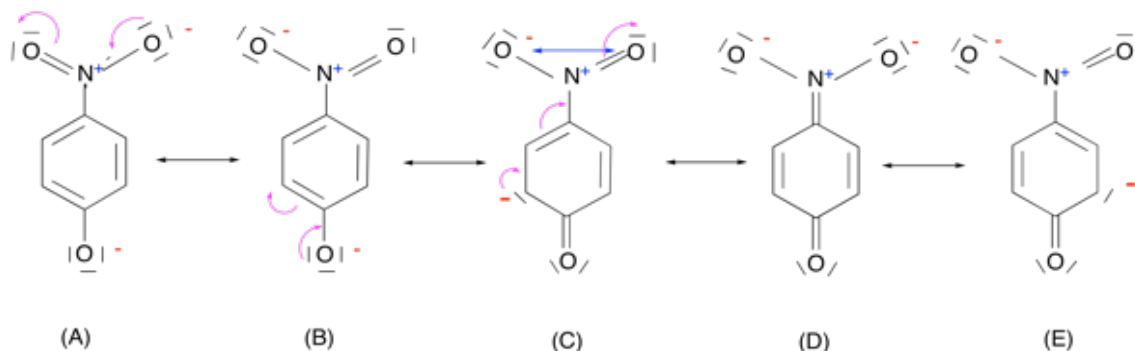


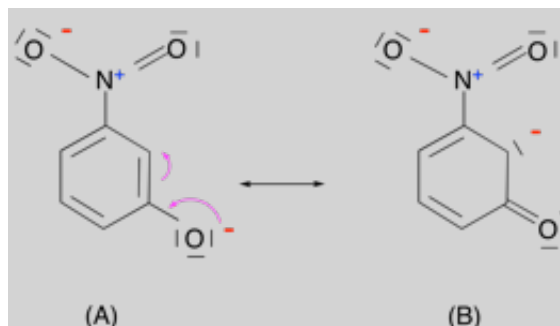
Figure 3.5 Resonance formulas of *p*-nitrophenoxide ion

Exercise 3.3 Resonance in *m*-nitrophenol

Confirm that, for *m*-nitrophenoxide ion, it is impossible to draw a resonance formula like (D) of *p*-nitrophenoxide ion.

Answer

For *m*-nitrophenoxide ion, the lone pair of oxygen atom can shift up to the benzene ring, but not to the nitro group. If you try to draw such a resonance formula forcibly, you have to make the carbon atom to which the nitro group is bonded pentavalent. The pK_a of *m*-nitrophenol is 9.82.



(3) Resonance effect in substituted benzoic acids

A nitro group which has strong $+I$ and $+R$ effects plays an important role in the acidity of benzoic acids as is the case with phenols. Thus, pK_a of nitrobenzoic acids shows the balance of $+I$ and $+R$ effects. $+I$ effect is observed at all of *ortho*-, *meta*- and *para*-positions, and the magnitude of the effect decreases in this order. On the other hand, $+R$ effect is observed only at *ortho*- and *para*-positions with nearly the same magnitude. The experimentally determined pK_a values are explainable in this way.

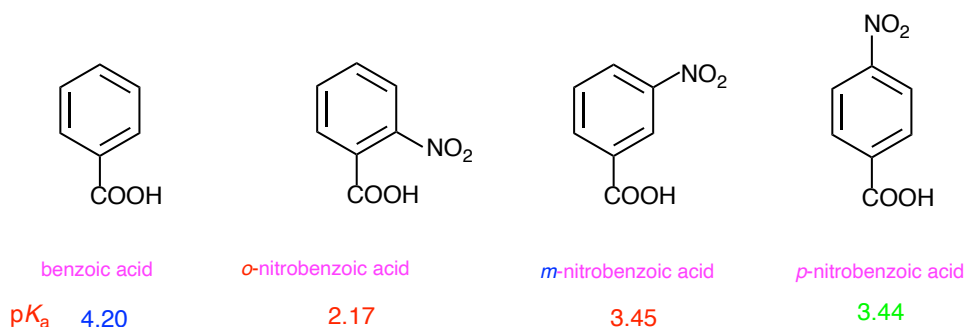


Figure 3.6 Acidity of substituted benzoic acids

(4) Classification of substituents

All substituents exert more or less electron-withdrawing or electron-donating inductive effects upon the mother moiety. Substituents without π -electron(s) or lone pair(s) do not exert neither $+R$ nor $-R$ effects. Whether the inductive and resonance effects of a substituent will be electron-withdrawing or electron-donating will depend on in part whether the substituent is bonded to the benzene ring directly or not.

If you understand the substituent effect, it will be helpful for you to understand the properties and reactions of organic compounds. In Table 3.3, the substituent effects so far discussed are tabulated. The substituents which are not discussed in this chapter will be treated in relevant chapters.

Point: Classification of substituent effects

Inductive effect (due to electronegativity)

electron-withdrawing ($+I$), electron-donating ($-I$)

Resonance effect (due to resonance)

electron-withdrawing ($+R$), electron-donating ($-R$)

Table 3.3 Substituent effects and their signs

substituent	inductive effect	resonance effect
$-\text{CH}_3$; methyl including alkyl groups in general	$-I$	$-R$
$-\text{CHO}$, $-\text{COR}$; aldehyde, keto	$+I$	$+R$
$-\text{COOH}$, $-\text{COOR}$; carboxylate and derivatives	$+I$	$+R$
$-\text{C}\equiv\text{N}$; cyano	$+I$	$+R$
$-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$; amino	$+I$	$-R$
$-\text{NO}_2$; nitro	$+I$	$+R$
$-\text{OH}$, $-\text{OR}$; hydroxy, alkyloxy, aryloxy	$+I$	$-R$
$-\text{OCOR}$; ester	$+I$	$-R$
$-\text{O}-$; ether	$+I$	$-R$
$-\text{X}$; halogens	$+I$	$-R$

$+$: electron withdrawing, $-$: electron donating

As for the (+) or (-) signs of inductive and resonance effects, there is a convention contrary to the one used in this textbook. Thus, in the alternative convention, the NO_2 group, for instance, has $-I$ and $-R$ effects rather than $+I$ and $+R$ effects. In the convention used in this book, the sign reflects the site of the decrease or increase of electron density caused by the substituents while in the other convention

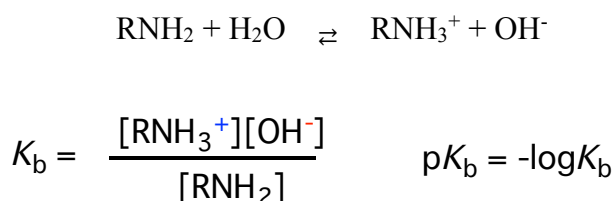
the sign reflects the decrease or increase of electron density of the substituents themselves.

According to the current Gold Book, IUPAC (<https://goldbook.iupac.org>), both sign conventions are in use. Those who are interested in this subject are kindly advised to consult the item “electronic effect of substituents: symbols and signs” in Gold Book.

3.5 Basicity of amines

(a) Basicity of alkylamines and arylamines

Though bases are treated rather briefly in Ch. 3.1, organic amines RNH_2 ($\text{R} = \text{alkyl or aryl}$) that play an important role in organic chemistry, will be treated in this section. In an aqueous solution, the basicity of amines is larger (K_b is larger and $\text{p}K_b$ is smaller) as the equilibrium shifts to the right side.



The basicity of amines in an aqueous solution is due to the coordination of the lone pair on nitrogen to proton. If the other part of the amine molecule donates electrons to the nitrogen atom, and increases the electron density of lone pair, the basicity increases. On the other hand, if the substituents withdraw electrons from the nitrogen atom, the electron density of the lone pair decreases and consequently the basicity decreases.

This point is exemplified by the large difference of basicity between alkylamines (*e.g.*, ethylamine $\text{C}_2\text{H}_5\text{NH}_2$; $\text{p}K_b = 3.25$) and arylamines (*e.g.*, aniline $\text{C}_6\text{H}_5\text{NH}_2$; $\text{p}K_b = 9.30$). Aniline is much weaker as a base as compared with ethylamine because in the former the lone pair on nitrogen is delocalized into the benzene ring.

The phenomenon discussed above is essentially identical with the resonance of phenoxide ion; that is, delocalization of lone pair electrons into benzene ring (Figure 3.7). Phenoxide ion is stabilized by the delocalization and the acidity of phenol is larger than that of ethanol. In the case of aniline, depolarization decreases the electron density of lone pair on nitrogen, and the basicity of aniline is weaker than that of ethylamine.

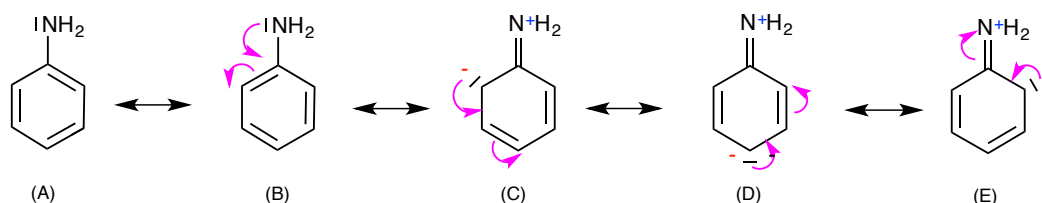
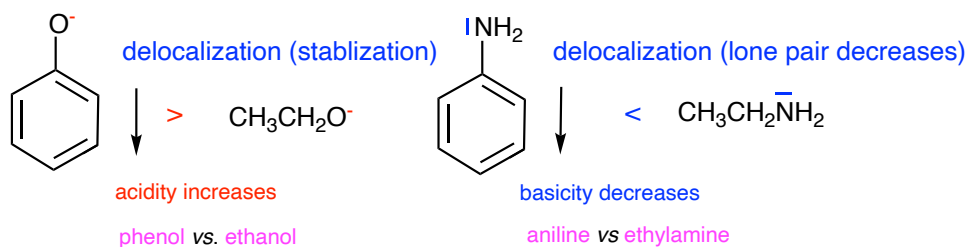


Figure 3.7 Resonance formulas of aniline

If the basicity of the conjugate acid BH^+ instead of using the basicity of the base B , the above discussion will become clearer. Due to the transfer of electrons, the acidity of anilinium ion $\text{C}_6\text{H}_5\text{NH}_3^+$ will become larger than that of ethylammonium ion $\text{CH}_3\text{CH}_2\text{NH}_3^+$ that is devoid of resonance effect.

You can understand why the amino group is classified as an electron donating group showing $-R$ effect if you consider the contribution of resonance formulas (C)-(E) in Figure. 3.7 (see Table 3.3).

Point: phenol vs. aniline**(b) Basicity of substituted anilines**

It is not difficult to predict the substituent effect on the basicity of substituted anilines if we know that the basicity of amines depends on the lone pair on the nitrogen atom. The basicity of anilines decreases by an electron-withdrawing substituent. The decrease is particularly large if electron withdrawing (+R) substituents are located at *ortho* or *para* positions.

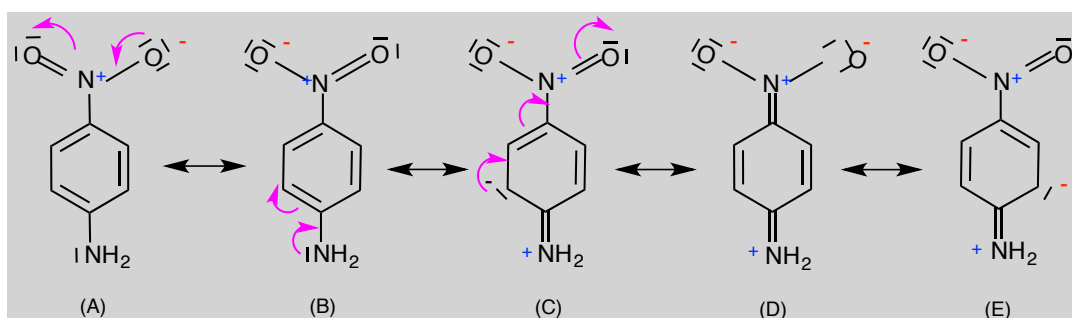
This prediction agrees well with the $\text{p}K_{\text{b}}$ data of *p*-nitroaniline ($\text{p}K_{\text{b}} = 13.01$) and *m*-nitroaniline ($\text{p}K_{\text{b}} = 11.40$).

Exercise 3.4 Basicity of *p*-nitroaniline

Explain the reason why the basicity of *p*-nitroaniline is smaller than that of aniline using resonance formulas.

Answer

In *p*-nitroaniline, there is a resonance formula (D) in which the lone pair shifts from nitrogen to nitro group *via* benzene ring in addition to resonance formulas (A) and (B) in which electrons shift within the nitro group, resonance formulas (C) and (E) in which electrons on the lone pair of nitrogen remain in the benzene ring.



Problems**3.1**

Draw the chemical formulas of conjugate acid and conjugate base of the following compounds.

- (a) H_2O (b) NH_3 (c) HCO_3^- (d) CH_3OH (e) $\text{C}_6\text{H}_5\text{NH}_2$, (f) H_2PO_4^-

3.2

The K_a value of acetic acid CH_3COOH is 1.8×10^{-5} and that of phenylacetic acid $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ is 4.9×10^{-5} . Decide whether a phenyl group is electron-donating or electron-withdrawing as compared with hydrogen.

3.3

Which one out of the pairs (a)-(d) is stronger as an acid? Explain the reason of your choice.

- (a) acetic acid and chloroacetic acid
 (b) benzoic acid and *p*-nitrobenzoic acid
 (c) phenol and ethanol
 (d) CH_3NH_3^+ and $\text{C}_6\text{H}_5\text{NH}_3^+$

3.4

Decide the order of strength of phenol, *p*-nitrophenol and picric acid as an acid. Give your reasoning based on the resonance formulas of corresponding phenoxide ions.

3.5

Decide the order of strength as an acid for each group of compounds.

- (a) $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, $\text{CH}_3\text{CHF}\text{COOH}$, $\text{CH}_3\text{CHBr}\text{COOH}$, $\text{BrCH}_2\text{CH}_2\text{COOH}$.
 (b) $\text{H}_3\text{N}^+\text{CH}_2\text{COOH}$, HOCH_2COOH , HSCH_2COOH .

Answers**3.1**

- (a) H_3O^+ , OH^- (b) NH_4^+ , NH_2^- (c) H_2CO_3 , CO_3^{2-} (d) CH_3OH_2^+ , CH_3O^-
 (e) $\text{C}_6\text{H}_5\text{NH}_3^+$, $\text{C}_6\text{H}_5\text{NH}^-$ (f) H_3PO_4 , HPO_4^{2-}

3.2

Since phenylacetic acid is a little more acidic than acetic acid, a phenyl group acts as an electron withdrawing group to stabilize the carboxylate ion.

3.3

- (a) chloroacetic acid > acetic acid ($\text{p}K_a = 2.68, 4.86$, +I effect of Cl)
 (b) *p*-nitrobenzoic acid > benzoic acid ($\text{p}K_a = 3.44, 4.20$, +I and +R effects of NO_2)
 (c) phenol > ethanol (resonance stabilization of phenoxide ion)
 (d) $\text{C}_6\text{H}_5\text{NH}_3^+$ > CH_3NH_3^+ (aliphatic amines are in general stronger as a base than arylamines.)

3.4

picric acid (0.33) > *p*-nitrobenzoic acid (3.44) > benzoic acid (4.20).

Resonance stabilization of phenoxide ion and *p*-nitrophenoxide ion is discussed in Figure. 3.1 and Figure 3.5. For picric acid, you can draw additional resonance formulas for two *ortho* nitro groups.

3.5

- (a) $\text{CH}_3\text{CHF}\text{COOH}$ > $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ > $\text{CH}_3\text{CHBr}\text{COOH}$ > $\text{BrCH}_2\text{CH}_2\text{COOH}$
 (b) $\text{H}_3\text{N}^+\text{CH}_2\text{COOH}$ > HOCH_2COOH > HSCH_2COOH

The electron attracting power of positive charge is very large.