

Acids and Bases: Molecular Structure and Acidity

Review the Acids and Bases Vocabulary List as needed.

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A. Introduction

There are approximately twenty million known organic compounds, but only a few thousand are listed in even the most extensive tables of pK_a values. How can we know the pK_a of a compound that is not on such a table? There are certainly many situations in which it would be impractical to synthesize the compound just to measure its pK_a (such as during an exam!).

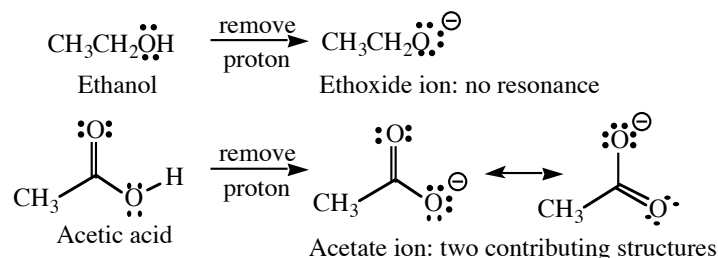
We have seen before that because similar functional groups react in similar ways that compounds with similar functional groups will have similar pK_a values. We can use this fact as a basis to predict trends in acidity or basicity. Recall that the role of a base is to share an electron pair with a proton, resulting in a new bond to that proton. A molecule that can donate electrons more readily will therefore be a stronger base. (There are some additional factors that we will not consider at this level.) Because we know that stronger bases have weaker conjugate acids, we can apply this same analysis to determine acidity as well. Many factors can influence a molecule's ability to donate electrons. The most common factors are resonance, atomic radius, electronegativity and the inductive effect. We consider each of these below. (These same factors also influence nucleophilicity.)

B. Resonance

A molecule is said to have resonance when its structure cannot be adequately described by a single Lewis structure. How does resonance influence the ability of a base to share electrons with a proton? Resonance may delocalize this the electron pair that the base might use to form the new bond with the proton. This delocalization increases the stability of the base. Greater stability results in lower reactivity. A base that has resonance delocalization of the electron pair that is shared with the proton will therefore be less basic than a base without this feature. Since a weaker base has a stronger conjugate acid, a compound whose conjugate base enjoys resonance stabilization will be more acidic.

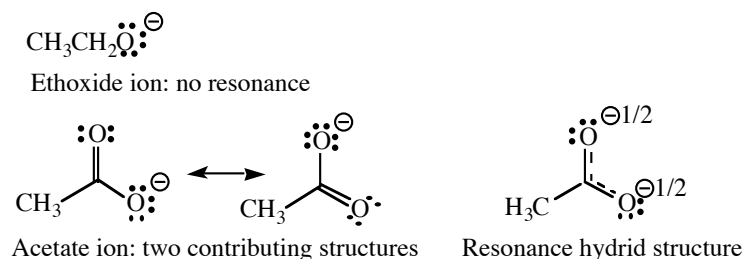
Example 1: Which O-H proton is more acidic, ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) or acetic acid ($\text{CH}_3\text{CO}_2\text{H}$)?

Solution: Acidity can readily be analyzed by examining the corresponding conjugate bases:



Deprotonation of ethanol affords ethoxide ion, which has no resonance (only one Lewis structure can be drawn). Deprotonation of acetic acid affords acetate ion that has resonance (two contributing Lewis structures can be drawn). Because acetate ion has resonance that delocalizes the electron pair to be shared with a proton and ethoxide ion does not, acetate ion is a weaker base than ethoxide ion. Recalling that weaker bases have stronger conjugate acids, we conclude that acetic acid is a stronger acid than ethanol. The actual $\text{p}K_a$ values agree with our prediction. For acetic acid the $\text{p}K_a$ is 4.76 (stronger acid) and for ethanol the $\text{p}K_a$ is 15.9 (weaker acid).

The resonance effect on $\text{p}K_a$ can be viewed in a variety of ways. For example, we can consider the magnitude of the charge on the atom(s) that would share an electron pair with a proton. An atom with greater charge has a higher incentive to stabilize this charge by sharing a pair of electrons with a proton. Thus, everything else being equal, an ion with more net charge per atom that shares an electron pair is a stronger base. Examination of the resonance hybrid structure for acetate ion suggests that the charge on each oxygen atom that would share an electron pair with a proton is $-1/2$. The charge on the oxygen of ethoxide ion is -1 . Because each oxygen atom of acetate ion has a smaller charge, it has less incentive to stabilize this charge by sharing an electron pair. Less incentive to share an electron pair with a proton means lowers basicity.

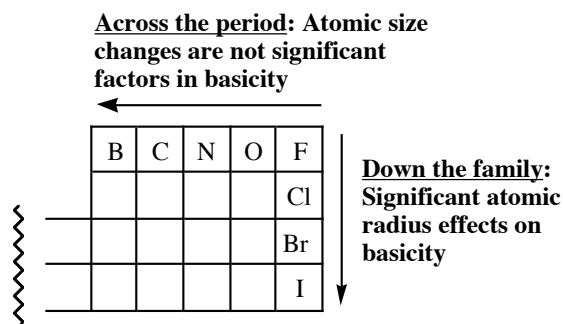


Alternately, recall that stability tends to increase with an increasing number of significant resonance contributors. Protonation usually results in loss of one or more of these resonance contributors. A base with many resonance contributors stands to lose more resonance than a base with a lesser number of resonance contributors. Thus a base with many resonance contributors will resist protonation (be a poorer base) than a similar structure with fewer resonance contributors. Acetate ion has two significant resonance contributors, and has more to lose upon protonation than ethoxide with a single resonance contributor. This analysis suggests acetate ion to be a poorer base than ethoxide ion, and thus acetic acid to be a stronger acid than ethanol.

C. Atomic Radius

Recall from fundamental electrostatics that atoms are most stable when their charges (positive or negative) are closest to neutral. In the case of a base, this neutrality can be achieved by sharing an electron pair (usually a lone pair) with a proton. The more concentrated the charge or electron density, the greater thermodynamic driving force there is to share electron density. This charge density is influenced by atomic radius. For an equal number of valence shell electrons, a smaller atom has greater charge density as measured by charge per unit of surface area or per unit of volume. Thus smaller atoms have a greater drive to share electron density.

How does atomic radius change between the elements? As we move down a family in the periodic table (i.e., second row to fifth row) atomic radius increases. Within a period (row) of the periodic table atomic size does vary but not enough to have a significant influence on basicity. (When comparing basicity influenced by two atoms in the same row of the periodic table, such as oxygen and nitrogen, electronegativity effects dominate. Electronegativity effects are discussed below.)



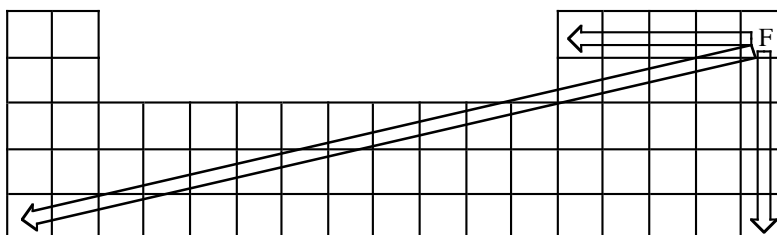
Example: Which is a stronger base, fluoride ion or iodide ion?

Solution: Consulting a periodic table reveals that fluorine is a second-row element whereas iodine is a fifth-row element, so F^- is a smaller ion than I^- . Both of these ions carry a -1 formal charge, but this charge on F^- is more concentrated than the charge on I^- . Thus F^- is a stronger base than I^- . The actual pK_a data support this conclusion: HF pK_a 3.2, HI pK_a -10. (Recall that stronger bases have weaker conjugate acids.)

D. Electronegativity

Recall that electronegativity is the measure of an atom's attraction for electrons. The higher the electronegativity, the greater the attraction. We can extend this idea further and conclude that atoms with higher electronegativity will be less inclined to share their electrons with a proton. Thus, increasing electronegativity of the atom that shares an electron pair will decrease basicity. Weaker bases have stronger conjugate acids, so we conclude that as electronegativity of an atom increases the acidity of the attached proton also increases.

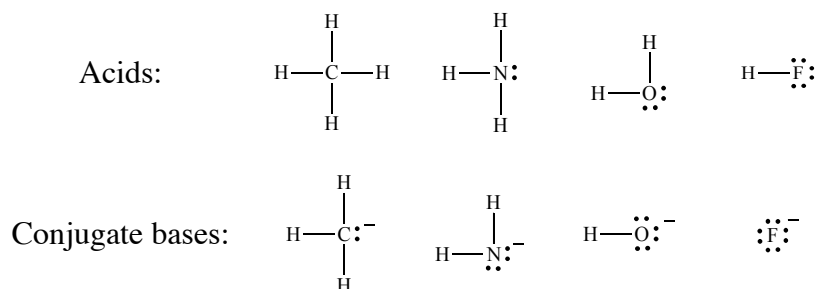
Electronegativity values can be found in the text. Linus Pauling devised the electronegativity scale that enjoys almost universal use today. On the Pauling scale, fluorine has the highest electronegativity (4.0) and cesium has the lowest (0.7). Electronegativity values generally do not need to be memorized, as study of the electronegativity table reveals a simple trend. As we move further away from fluorine on the periodic table, electronegativity decreases. The exception to this is the noble gases, which have essentially zero electronegativity.



Electronegativity decreases with increasing distance on the periodic table from fluorine.

Example: Rank the following compounds in order of increasing acidity without using a pK_a table: CH_4 , NH_3 , H_2O , HF .

Solution: Convert each acid to its conjugate base, and consider the ability of that conjugate base to share an electron pair.



The lone pairs that are shared with a proton reside on C, N, O, and F. Of these, carbon is the least electronegative (most willing to share electrons), so CH_3^- (methide ion) is the strongest base. Fluorine is the most electronegative, so F^- (fluoride ion) is the least willing to donate electrons (the weakest base). Overall, the electronegativity order is $\text{C} (2.5) < \text{N} (3.0) < \text{O} (3.5) < \text{F} (4.0)$, so the order of basicity is CH_3^- (strongest base) $> \text{NH}_2^- > \text{HO}^- > \text{F}^-$. The relationship between conjugate basicity and acidity is an inverse one, so the order of acidity is: CH_4 (weakest acid) $< \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$ (strongest acid). The actual pK_a values agree with this prediction: CH_4 pK_a 51 (weakest acid), NH_3 pK_a 38, H_2O pK_a 15.7 and HF pK_a 3.2.

E. Inductive Effect

We have seen the effect of differences in the electronegativity or charge of the atom that shares a pair of electrons with a proton. What effect on basicity is seen when the structural differences are not limited to the atom sharing the electron pair?

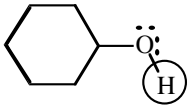
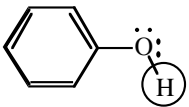
Example: How is the acidity of acetic acid (CH_3COOH) changed when one of the methyl group hydrogens is replaced by a chlorine atom to make chloroacetic acid (ClCH_2COOH)? Alternately, what does this do to the relative basicity of acetate ion (CH_3CO_2^-) versus chloroacetate ion ($\text{ClCH}_2\text{CO}_2^-$)?

Solution: This structural difference does not change the electronegativity or atomic radius of the oxygen atoms that share an electron pair with a proton, nor does it change the number of resonance contributors. A new explanation is in order. Recall that the role of a base is to share an electron pair with a proton to form a new covalent bond. The less electron density available (i.e. less negative charge), the harder it is for the atom to share this electron pair. What effect does the replacement of hydrogen with chlorine have on the electron density of the oxygen atoms? Chlorine is more electronegative than carbon, so the chlorine pulls electron density from the adjacent carbon atom. This carbon atom in turn borrows electron density from the neighboring carbonyl carbon, and so forth. The end effect is that the chlorine atom pulls electron density toward itself and away from the CO_2^- (carboxylate) group. The reduced electron density of the carboxylate group means lower basicity. Thus we predict $\text{ClCH}_2\text{CO}_2^-$ to be a poorer base than CH_3CO_2^- , and by extension, ClCH_2COOH to be a stronger acid than CH_3COOH . The actual $\text{p}K_a$ values are 2.86 for ClCH_2COOH (stronger acid) and 4.76 for CH_3COOH (weaker acid). (You can read more about the inductive effect and the $\text{p}K_a$ of carboxylic acids in the text chapter on carboxylic acids.)

The effect of one atom or group of atoms on the electron density on a remote portion of the molecule is called the *inductive effect*.

F. Exercises

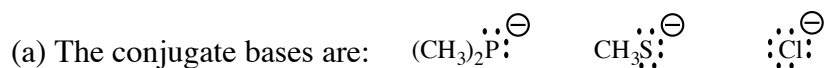
Without relying on a $\text{p}K_a$ table, rank each set of compounds in order of decreasing acidity. Where the molecule contains more than one type of hydrogen atom, the most acidic hydrogen atom is circled.

- (a) $(\text{CH}_3)_2\ddot{\text{P}}-\text{H}$ $\text{CH}_3\ddot{\text{S}}-\text{H}$ $:\ddot{\text{Cl}}-\text{H}$ (e) $\text{FCH}_2\text{CO}_2-\text{H}$ $\text{BrCH}_2\text{CO}_2-\text{H}$ $\text{ClCH}_2\text{CO}_2-\text{H}$
- (b) $\text{CH}_3\text{CH}_2\text{N}(\text{H})_2$ $\text{CH}_3\text{C}(=\text{O})\text{N}(\text{H})_2$ (f) H_3O^+ $\text{H}_3\text{C}-\text{O}^+(\text{H})_2$
- (c)   (g) $\text{H}_2\text{S}, \text{H}_2\text{O}$
- (d) $\text{NH}_4^+, \text{H}_3\text{O}^+$

Solutions are on the next page.

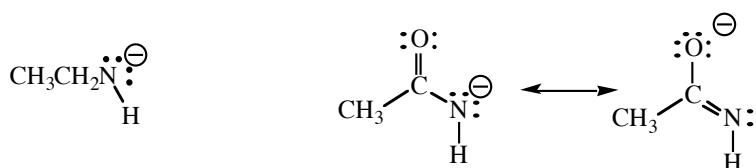
G. Exercise Solutions

In each case, we remove the circled proton and then consider the ability of the conjugate base to donate electrons to a proton. Because stronger conjugate bases come from weaker acids, the acidity ranking will be reverse of the basicity ranking.



There is a difference in electronegativity between the three atoms that would share electrons. Chlorine is most electronegative (3.0), followed by sulfur (2.5) and phosphorus (2.1). Chloride ion has the greatest resistance to sharing an electron pair and thus is the poorest base. The phosphide ion, $(\text{CH}_3)_2\text{P}^\ominus$, has the least resistance to sharing an electron pair, and thus is the strongest base. Order of basicity: Cl^\ominus (weakest base) < $\text{CH}_3\text{S}^\ominus$ < $(\text{CH}_3)_2\text{P}^\ominus$ (strongest base). Order of acidity: HCl (strongest acid) > CH_3SH > $(\text{CH}_3)_2\text{PH}$ (weakest acid).

(b) The corresponding conjugate bases are:

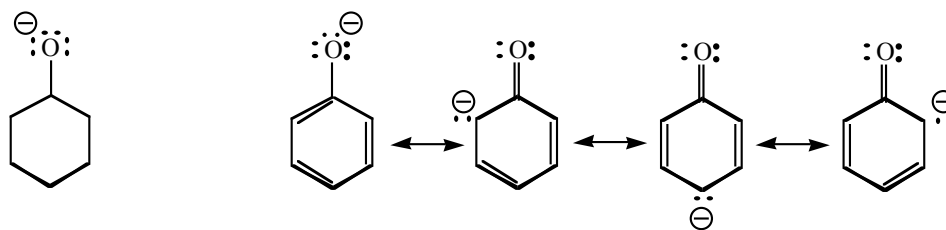


Only one resonance contributor

Two resonance contributors

The conjugate base of $\text{CH}_3\text{CH}_2\text{NH}_2$ (ethylamine) has a single resonance contributor, whereas the conjugate base of the amide has two resonance contributors. The presence of resonance stabilizes the conjugate base, making it a weaker base. Because a weaker conjugate base is derived from a stronger acid, we conclude that the amide is a stronger acid than the amine.

(c) The corresponding conjugate bases are:

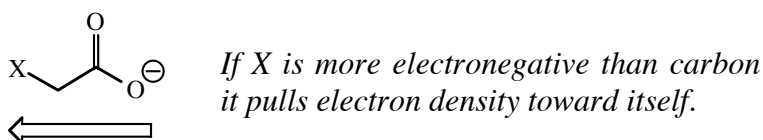


One resonance contributor

Four resonance contributors

The conjugate base of cyclohexanol ($\text{C}_6\text{H}_{11}\text{OH}$) has a single resonance contributor, whereas the conjugate base of phenol ($\text{C}_6\text{H}_5\text{OH}$ or PhOH) has four resonance contributors. Because the conjugate base of phenol has more resonance contributors, phenol is more acidic than cyclohexanol.

- (d) The corresponding conjugate bases are ammonia (NH_3) and water. Resonance is not an issue in this case. Ammonia accepts a proton by sharing the nitrogen lone pair. Water accepts a proton by sharing an oxygen lone pair. Nitrogen is less electronegative than oxygen and would be more willing to share the lone pair. Thus ammonia is a stronger base than water, and ammonium ion (NH_4^+) is a weaker acid than hydronium ion (H_3O^+).
- (e) All three protons are removed from the same functional group, a carboxylic acid. The conjugate bases all have two resonance structures. Since each conjugate base would take a proton by sharing electrons from an oxygen atom. The conjugate bases are therefore almost identical. This is because they are derived from exactly the same functional group! The only difference between these three acids is the halogen atom (fluorine, bromine, or chlorine). Because these atoms are not directly involved in sharing electrons with a proton, we consider their inductive effects. (Any time you are considering the acidity of identical functional groups, you can skip immediately to inductive effects for this same reason.) The conjugate base of a carboxylic acid is a carboxylate ion $\text{XCH}_2\text{CO}_2^-$ ($\text{X} = \text{F}, \text{Cl}, \text{or Br}$). If the X group is more electronegative than carbon, it pulls electron density from the rest of the molecule toward itself.



This effect decreases the electron density and charge on the oxygen atoms that would share a lone pair with a proton. This decrease in electron density on the oxygen atoms decreases the strength of the base. The magnitude of this electron density shift depends on the electronegativity of X. The greater the electronegativity, the more electron density is removed from the carboxylate group, and the lower the basicity becomes. Of the three X groups in this case, fluorine is the most electronegative, so $\text{FCH}_2\text{CO}_2^-$ is the weakest base. Bromine is the least electronegative, so $\text{BrCH}_2\text{CO}_2^-$ will be the strongest base. The order of acidity is reverse of the order of conjugate base strength, so the relative acidity ranking is: $\text{FCH}_2\text{CO}_2\text{H}$ (strongest acid) $>$ $\text{ClCH}_2\text{CO}_2\text{H}$ $>$ $\text{BrCH}_2\text{CO}_2\text{H}$ (weakest acid).

- (f) The conjugate bases are water (HOH) and CH_3OH (methanol). In both cases, the functional group that would share an electron pair with a proton is a HO group. Because these are the same functional group, we need only consider inductive effects. The difference between these structures is a hydrogen atom for water versus a methyl group (CH_3) for methanol. Neither is very electronegative, so we expect then to have little if any effect on the electron density at oxygen. (Alkyl groups such as methyl groups are weak electron donors, as we will see when we discuss carbocations). We conclude there is little difference in the electron density of the oxygen atom in water and methanol. Therefore they are of similar basicity, and by extension, the conjugate acids will have similar $\text{p}K_a$ values.
- (g) The conjugate bases are HS^- (hydrosulfide ion) and HO^- (hydroxide ion). Sulfur (third row of the periodic table) has a larger atomic radius than oxygen (second row). Thus the negative charge is less concentrated on HS^- than on HO^- . A lower charge concentration makes HS^-

and weaker base than HO^\ominus . Recall that weaker bases have stronger conjugate acids, so H_2S (hydrogen sulfide) is a stronger acid than H_2O .