

CHEM 346 – Organic Chemistry I (for Majors)

Instructor: Paul J. Bracher

Practice Hour Examination #1-1Monday, September 9th, 2013
1:10 p.m.

Student Name (Printed)	Solutions
Student Signature	

Please also write your name on the back of the exam

Scoring

Question	Points Earned	Points Available
1		15
2		25
3		30
4		20
TOTAL		90

Original Problems, **Required Information in Answers**, and **Supplementary Explanation**

Problem 1. (15 points total, 3 points each) Determine whether the following five statements are true or false. Write out the full word “true” or “false” beside each statement; do not just write “T” or “F”. If any part of the statement is false, the entire statement is false.

- (i) FALSE Boron trifluoride (BF_3) is a strong Lewis base, but does not typically act as a Brønsted–Lowry base.

While it is true that BF_3 does not “typically” act as a Brønsted–Lowry base by accepting a proton—I’ve never seen it—the molecule is certainly not a “strong” Lewis base. Strong Lewis bases possess nucleophilic electron pairs (usually, lone pairs or π bonds) that can be donated to Lewis acids to form a new σ bond. The lone pairs in BF_3 reside with fluorine atoms, which typically do not like to donate electrons or assume positive formal charges. Rather, BF_3 is an excellent Lewis acid (not base), owing to the presence of an empty unhybridized p orbital on boron.

- (ii) TRUE Water (H_2O) can serve as both a Lewis acid and a Lewis base.

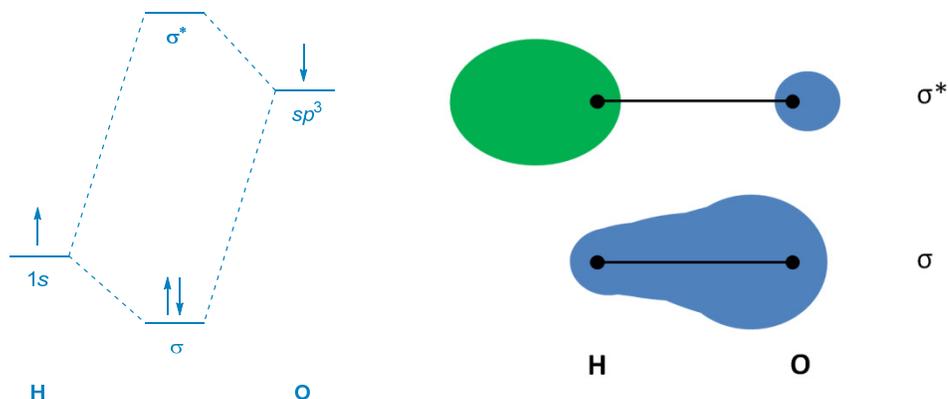
We know water can act as both a Brønsted–Lowry acid (by giving up a proton to form HO^-) or a Brønsted–Lowry base (by accepting a proton to form H_3O^+). Since all Brønsted–Lowry acids and bases are also Lewis acids and bases, respectively, the answer to this question must be “true”.

However, you are probably used to thinking of Lewis acids as molecules capable of accepting electron pairs to form new σ bonds and Lewis bases as molecules capable of donating electron pairs to form new σ bonds. How does water fit into this model?

Well, it is straightforward to see how water can act as a Lewis base. The oxygen atom has two lone pairs in different sp^3 orbitals, either of which can be used to attack a Lewis acid and form a new σ bond.

It is, perhaps, less straightforward to see how water can act as a Lewis acid. Let’s take a closer look at the bonds between the central oxygen and the two hydrogen atoms. These bonds are formed when a half-filled $1s$ orbital on hydrogen interacts with a half-filled sp^3 orbital on oxygen. (Actually, molecular orbital theory is much more complicated than this, but the simplification is useful.)

You must remember that whenever you mix two orbitals together, you will generate two new orbitals. The overlap of orbitals generates constructive interference corresponding to a new σ -bonding molecular orbital, and destructive interference corresponding to a new σ^* -antibonding molecular orbital. The two electrons fill the bonding orbital and are stabilized relative to when they simply resided in the atomic orbitals on the atoms (see below). The shape of the bonding orbital should be fatter around oxygen because we know that oxygen is more electronegative than hydrogen and will pull more of the negative charge density toward itself.



The antibonding orbital is empty but still present. It has the (roughly drawn) shape pictured above, with lobes located mostly behind the axis of the bond (where if the orbital were filled, the electron-density would cancel the bonding interaction). Since the lobe of the bonding orbital is bigger near oxygen, the lobe near hydrogen must be bigger in the antibonding orbital (to conserve the character of the atomic orbitals that mixed to form the bond.) This fat lobe of the empty σ^* orbital is what makes the hydrogen atom a Lewis acid (or an electrophilic site on the molecule). An electron pair donated into the lobe of σ^* behind hydrogen will simultaneously break the H–O bond and form a new σ bond between the hydrogen and the incoming base.

- (iii) FALSE Sodium hydroxide (pK_a of conjugate acid = 15.7) cannot deprotonate acetone ($pK_a = 20$)

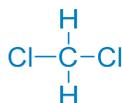
This question was pulled right from the lecture slides as an example of a “fail” by the authors of the textbook material. Do not confuse “cannot deprotonate” with “disfavors deprotonation”.

Yes, the proton-transfer reaction of hydroxide with acetone strongly disfavors the products, with an equilibrium constant of only $\sim 10^{-4.3}$, but that means that something between 1 in 10,000–100,000 molecules of acetone will be deprotonated in the mixture. If these deprotonated acetone molecules form and react quickly, the deprotonation could be very important to driving a chemical reaction. This is exactly what happens in the aldol reaction, which we will discuss next semester.

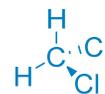
- (iv) FALSE While the individual bonds in methylene chloride (CH_2Cl_2) are polar, the molecule has no net dipole moment.

The individual bonds in methylene chloride are polar, as no bond has the same atom or group of atoms on either side, but the dipoles (which are vectors) corresponding

to each of the four bonds do not add up to zero. To see why, we must draw a three-dimensional Lewis structure for the molecule:



not a great way to draw CH_2Cl_2
(the molecule is not square planar)

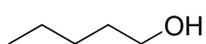


a better way to draw CH_2Cl_2
(the molecule is tetrahedral)

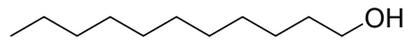
If you were to draw methylene chloride using the Lewis structure on the left, you might think that the dipole moments of the bonds cancel exactly. But we know that carbon bonded to four atoms is sp^3 hybridized and prefers bond angles near 109.5° , not 90° . The Lewis structure on the right is more accurate in that it conveys the tetrahedral structure of methylene chloride. In this structure, it is clear that the dipole moments of the individual bonds do not cancel.

(v) FALSE

1-undecanol, drawn below, has a lower melting point than 1-pentanol.



1-pentanol

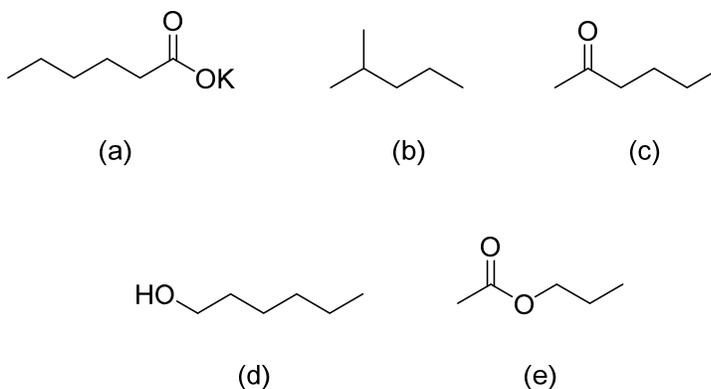


1-undecanol

1-Undecanol has a higher melting point than 1-pentanol. The melting point of a compound is determined primarily by the strength of its intermolecular interactions and then by how well it packs into a crystal phase. Both compounds have single hydroxyl groups and are unbranched. The longer hydrocarbon chain of the undecanol exposes more surface area for the generation of favorable London forces (induced dipole–induced dipole interactions). Everything else being roughly similar, undecanol should have stronger intermolecular interactions, and thus, a higher melting point. As it turns out, the melting point for 1-pentanol is -78°C while that for 1-undecanol is 19°C .

Problem 2. (25 points total, 5 points each) For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided.

(i) A Which of the following molecules has the highest solubility in water?



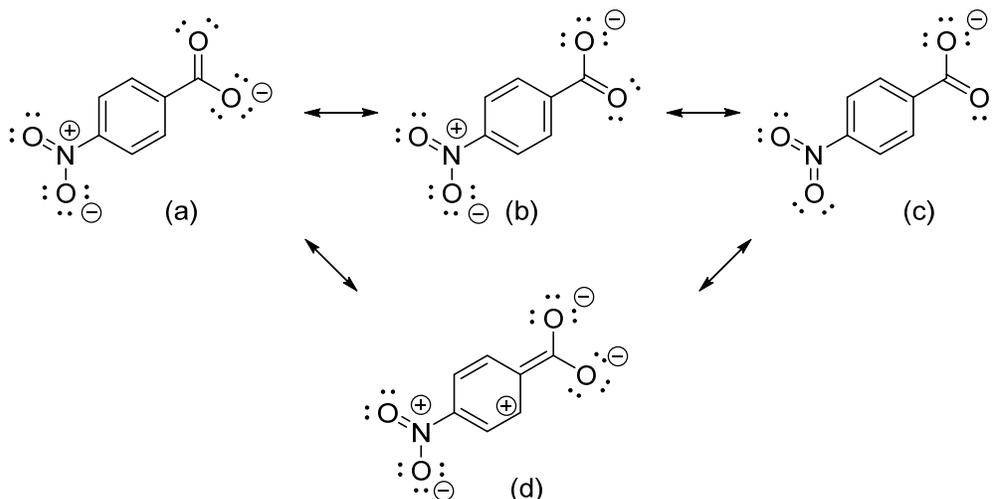
The general rule of thumb is that “like dissolves like”, and molecules with more polar or charged groups typically have higher solubilities in water. Here, the molecules are all roughly similar in size, so we can focus on the differences in their functional groups. Of the candidates, compound (d) looks promising for its ability to both donate and receive hydrogen bonds with water, but compound (a) is ionic, introducing the possibility of stronger ion–dipole interactions with water. Compound (a) should have the highest solubility of the choices.

(ii) D Which of the following molecules is the most polar?

- (a) H₂
- (b) BH₃
- (c) CH₄
- (d) NH₃
- (e) F₂

The only molecule with a net dipole moment is NH₃, ammonia. H₂ and F₂ are diatomic and obviously nonpolar (since the bonds are between atoms of the same element). BH₃ and CH₄ have symmetrical structures where the dipoles of the bonds cancel each other exactly and leave no residual net dipole moment. BH₃ is trigonal planar with sp²-hybridized boron, while CH₄ is tetrahedral with an sp³-hybridized carbon. The nitrogen in NH₃ is also sp³-hybridized; it is bonded to four structural pairs (3 σ bonds with hydrogen and 1 lone pair). The asymmetry in the molecule prevents the dipoles from canceling exactly, so ammonia is polar.

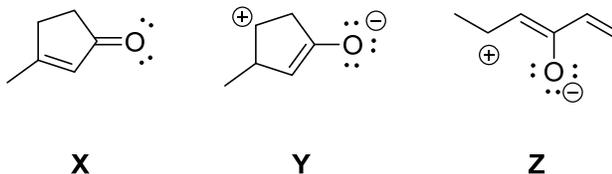
- (iii) C Which of the following resonance forms will have the least contribution to the resonance hybrid of the *p*-nitrobenzoate anion?



The more favorable a resonance form is, the greater contribution we expect it to have to the resonance hybrid—the true electronic distribution in the molecule the resonance forms collectively attempt to describe. More favorable resonance forms typically (i) give elements a full octet, (ii) avoid needless generation of formal charges, (iii) place any negative formal charges on electronegative atoms, and (iv) avoid the placement of positive charges on electronegative atoms.

Here, (a) and (b) are equivalent resonance forms that favorably place the negative charge in the anion on oxygen, which is more electronegative than carbon. Resonance form (d) is less favorable than (a) and (b) in that it introduces more separation of charge. Where (c) might appear more favorable than the other structures because it reduces separation of charge, it does so in a manner that gives the nitrogen atom five bonding pairs and more than a full octet. This would require nitrogen to access its 3*d* orbitals, which are too energetically inaccessible. Thus, (c) is an invalid Lewis structure and will not contribute any character to the resonance hybrid.

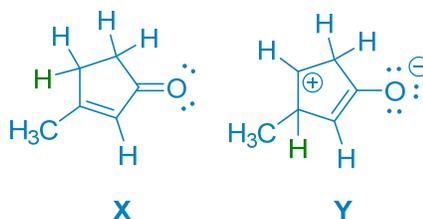
- (iv) **B** Choose the most correct and complete statement about the following Lewis structures:



- (a) Structures **X** and **Y** are resonance forms
 (b) Structures **X** and **Z** are isomers
 (c) Structures **Y** and **Z** are resonance forms
 (d) Statements (a) and (b) are both true
 (e) Statements (a), (b), and (c) are all false

Two molecules are isomers if they have the same molecular formula (i.e., same number of each type of atom) and the same number of electrons. Two Lewis structures are resonance forms if they have the same arrangement of atoms in space and only differ by how electrons are distributed among overlapping orbitals (typically π bonds and lone pairs). The best way to approach this problem is to judge first the veracity of statements (a), (b), and (c).

Statement (a) is false because not all of the hydrogen atoms are in the same position in structures **X** and **Y**. This may be hard to see because the location of hydrogens are not marked explicitly in skeletal structures. You may want to draw out the implied hydrogens to help you answer these types of questions.



(different arrangement of atoms = not resonance forms)

Statement (b) is true. Both structures **X** and **Z** have the molecular formula C_6H_8O , the same overall charge (zero), and a different arrangement of atoms (so they are not resonance structures). These traits make them isomers.

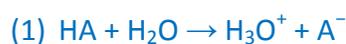
Statement (c) is false. You can tell by inspection that the atoms don't have the same connectivity of σ bonds, so they cannot be resonance forms.

Statement (d) is false because (a) is false. Statement (e) is false because (b) is true. Therefore, (b) is the best answer.

(v) A Benzoic acid has a pK_a of 4.2 in water. In a dilute aqueous solution buffered at pH 6.2, approximately what percentage of a sample of benzoic acid will be deprotonated?

- (a) 99% deprotonated
- (b) 91% deprotonated
- (c) 50% deprotonated
- (d) 9% deprotonated
- (e) 1% deprotonated

The important equations to remember here are:



(2) $K_a = ([H_3O^+][A^-])/[HA]$

(3) $pK_a = -\log K_a$

(4) $pH = -\log [H_3O^+]$

Rearrangement of (2) gives:

$$[A^-] / [HA] = K_a / [H_3O^+]$$

Further substitution with (3) and (4) gives:

$$[A^-] / [HA] = 10^{-pK_a} / 10^{-pH} = 10^{pH-pK_a}$$

So at $pH = pK_a$, an acid should be 1:1 deprotonated to protonated (or 50%).

At a pH 1 unit higher than an acid's pK_a , the acid should be 10:1 deprotonated (91%).

At a pH 2 units higher than the pK_a , an acid should be 100:1 deprotonated (99%).

Notice that for each pK_a unit of difference, the fraction of deprotonated acid changes by an order of magnitude. This is because the pH and pK_a scales are based on logarithms of base 10.

Problem 3. (30 points total) Consider the molecules benzene (C_6H_6) and cyclohexane (C_6H_{12}).

- (i) (8 points) Draw Lewis structures for benzene and cyclohexane given the fact that every carbon in each molecule has the same number of hydrogens bound to it.

When you are given a molecular formula and asked to draw a Lewis structure, it is generally best to start by calculating the degree of unsaturation (Ω) for each molecule:

$$\Omega = \frac{2 + 2(\text{\# of C's}) + (\text{\# of N's}) - (\text{\# of H's}) - (\text{\# of X's})}{2}$$

$$\Omega \text{ for } C_6H_6 = 4$$

$$\Omega \text{ for } C_6H_{12} = 1$$

The degree of unsaturation lets you determine how many rings and π bonds are in the molecule. Note that the presence of oxygen does not factor into the calculation. Halogens ($X = F, Cl, Br, \text{ or } I$) count the same as hydrogens.

The problem stipulates that every carbon is equivalent in the structure of C_6H_{12} . This fact, along with the calculation of $\Omega = 1$ —meaning that there is only one ring or π bond in the molecule—suggests that the structure is cyclic. (Also, note that it is named *cyclohexane*.) The equivalence of the carbons in C_6H_6 also suggests a ring, and the high degree of unsaturation suggests a ring with 3 π bonds:



benzene
 C_6H_6

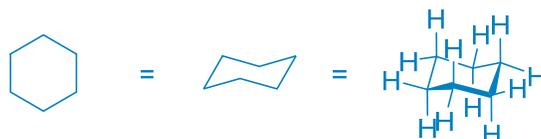


cyclohexane
 C_6H_{12}

- (ii) (8 points) Do you expect all of the carbon atoms of each molecule to lie in the same plane? Explain.

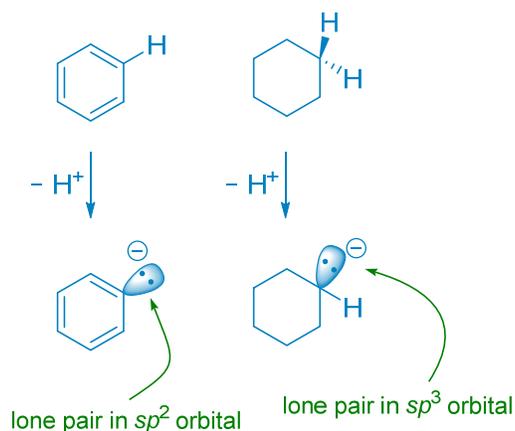
The carbons in benzene are coplanar. The carbons in cyclohexane are not.

The skeletal structures drawn above all show the carbons as lying in the same plane with bond angles (drawn) as 120° . The carbons of benzene are all sp^2 hybridized and should prefer bond angles of 120° . Thus, it makes sense for benzene to be planar. The carbons in cyclohexane are sp^3 hybridized and should prefer bond angles of 109.5° . Forcing the $C_{sp^3}-C_{sp^3}$ bonds to adopt bond angles of 120° would introduce a tremendous amount of strain. The only other solution to generate a cyclic structure for C_6H_{12} would be for the carbons to not be coplanar, as drawn here:



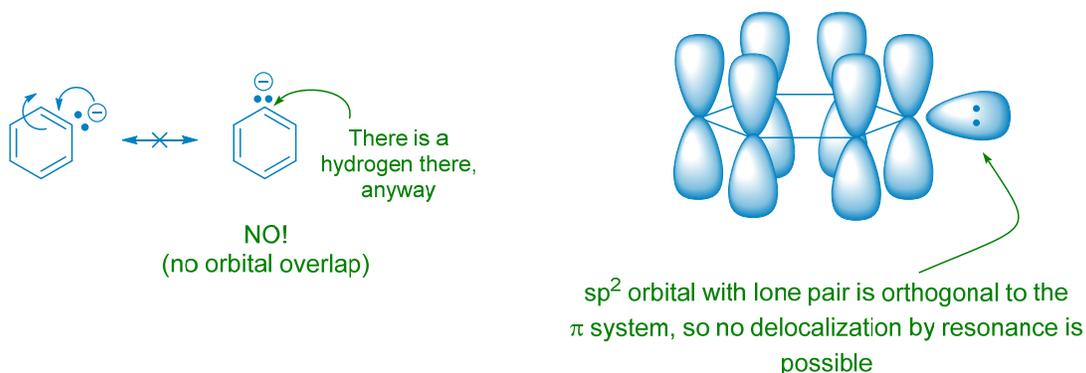
(iii) (8 points) Which of the compounds is the stronger Brønsted–Lowry acid? Explain.

To assess the relative ability of two similar molecules to act as acids, we should compare the relative stabilities of the conjugate bases. We would expect that the stronger acid to produce a more stable conjugate base (vs. the conjugate base of the other acid). Remember, Brønsted–Lowry acids are molecules that donate protons (H^+):



When benzene behaves as a Brønsted–Lowry acid, the residual lone pair on the conjugate base is placed in an sp^2 orbital. When cyclohexane behaves as a Brønsted–Lowry base, the residual lone pair resides in an sp^3 orbital. Electron density tends to be stabilized in orbitals with more s character (than p character), and sp^2 orbitals (33% s -character) stabilize electron density better than sp^3 orbitals (25% s -character). As a result, the conjugate base of benzene is more stable than that of cyclohexane, so benzene is the stronger Brønsted–Lowry acid.

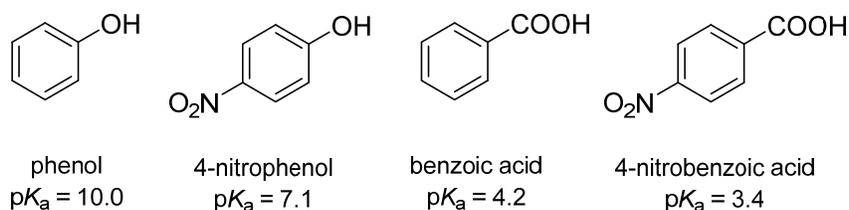
It is very important to note that the negative charge on the conjugate base of benzene cannot be delocalized by a resonance effect. Delocalization via resonance effects can only take place through overlapping orbitals. In deprotonated benzene, the orbital with the lone pair does not overlap constructively with the π system of the ring. Be careful about how you “push” electrons in Lewis structures!



(iv) (6 points) Which of the compounds is the stronger Lewis base? Explain.

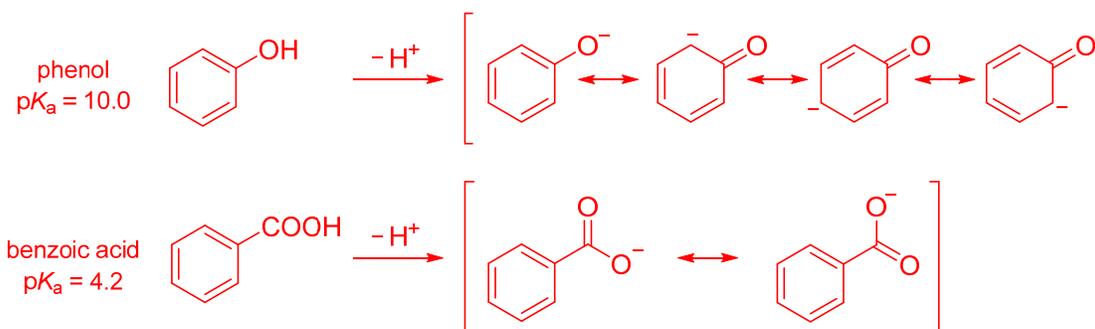
Lewis bases have electron pairs capable of forming new σ bonds to Lewis acids. All of the valence electrons in cyclohexane are held in σ bonds, which are not especially available to serve as nucleophiles. Benzene, on the other hand, has electron pairs in three π bonds. These electrons are less stabilized and more available to serve as nucleophiles. Thus, benzene is the stronger Lewis base.

Problem 4. (20 points total) Consider the following four molecules and their pK_a values in water.



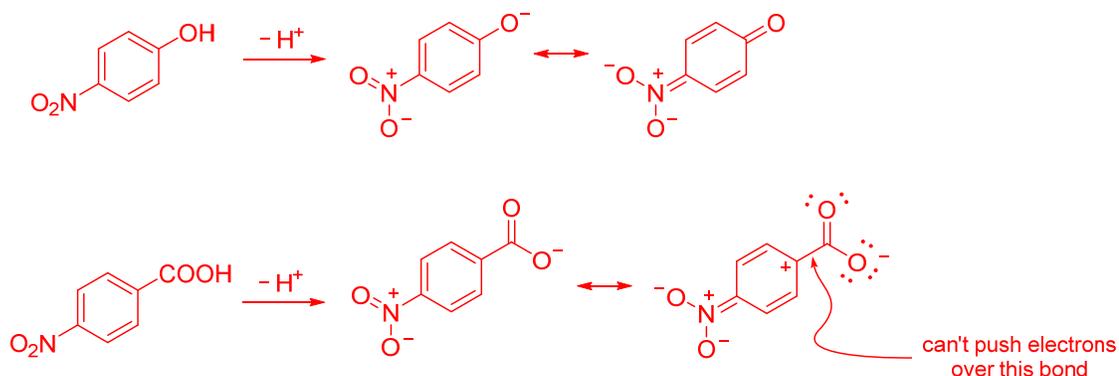
(i) (8 points) Explain why benzoic acid is a stronger acid than phenol. Hint: You're going to want to draw things here.

When comparing two structurally similar acids, it is often easiest to judge their relative acidity by judging the relative stabilities of the conjugate bases. The more stable the conjugate base, the easier it should be to form—meaning the acid is more acidic.



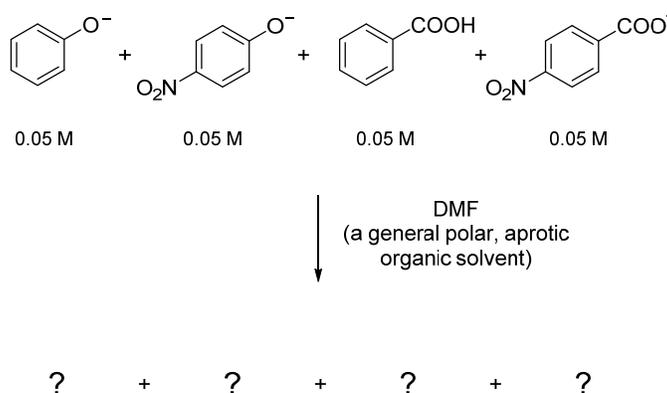
Drawn above are resonance structures for the conjugate bases of phenol and benzoic acid. While one may draw four resonance structures for the favorable delocalization of the negative charge in phenol, three of these structures place the extra negative charge on carbon (which is not especially electronegative). In contrast, the conjugate base of benzoic acid has the negative charge delocalized over two electronegative oxygen atoms. Apparently, this difference is what makes benzoic acid a much stronger acid than phenol.

(ii) (8 points) Explain why adding the nitro group at the 4 position of the phenyl group has a much more significant impact on the acidity of phenol (~3 orders of magnitude) relative to benzoic acid (<1 order of magnitude).



The presence of the nitro group at the 4-position of phenol allows the negative charge on the phenolate to be delocalized onto an electronegative oxygen atom in the nitro group by a resonance effect. This extra stabilization of the conjugate base explains why 4-nitrophenol is a much stronger acid than phenol. For the analogous situation with 4-nitrobenzoic acid, the negative charge on the carboxylate in the conjugate base cannot be “pushed all of the way” onto the nitro group. (Try drawing a valid Lewis structure to do so—you cannot). Rather, the most the nitro group can help by a resonance effect is by withdrawing electron density from the ring, which in turn, can help stabilize the carboxylate by an inductive effect. This stabilization of the conjugate base is less pronounced, so the effect on acidity is less pronounced than for the nitro-substitution of phenol.

(iii) (4 points) Predict the major product of the following proton-transfer reaction:



If you couldn't tell by inspection, the reaction that is taking place here is the simple transfer of protons among these molecules. The use of an aprotic solvent means the solvent cannot supply additional protons, so the 0.05 M benzoic acid is the only source of protons. (Everything else is already deprotonated.)

Every molecule is present at the same concentration, which makes the analysis easier—the strongest base will get the 0.05 M of protons. The strongest base will have the weakest conjugate acid (highest pK_a). Here, that is phenol, so the answer is:

