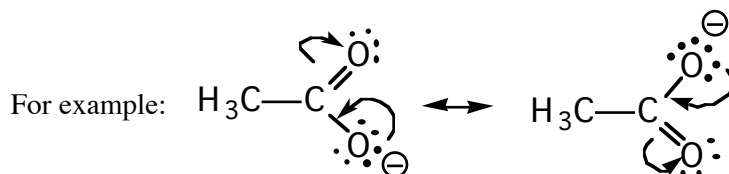


## Resonance Structures

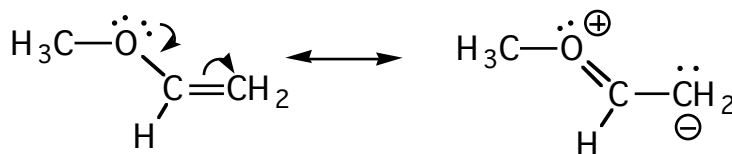
### Arrow Pushing Practice

The following is a collection of ions and neutral molecules for which several resonance structures can be drawn. For the ions, the charges can be delocalized implying greater stability; for the neutral molecules, electrons can be shuffled around to show areas of high or low electron density. Use electron arrows to show how one resonance structure can be transformed into another.

In this example, a lone pair of electrons on an O atom is delocalized onto another O atom through the  $\pi$ -system as shown. Note that the arrows start at a pair of electrons. These resonance structures are used to explain the acidity of the carboxylic acid functional group.



The resonance structures below show how a charge-separated resonance structure can be drawn for a neutral molecule. This additional resonance structure suggests that the electron density is high on the carbon that bears a negative charge. Indeed, there is spectroscopic evidence that confirms this and this carbon acts as a nucleophile in many reactions. Note that the electron pushing is identical to that in the example above.

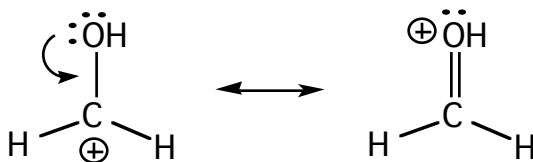


The following resonance structures depict the allyl cation. Allyl cations are relatively stable (as cations go) due to delocalization of the positive charge. In this case, the  $\pi$ -electrons move towards the electron deficient carbon atom. Again, the arrow starts at an electron pair - the  $\pi$ -electrons in this case.

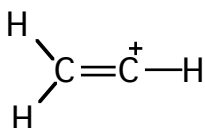


Look for the similarities in these electron movement processes. There are only three basic kinds of electron movements in all of these examples: movement of a lone pair of electrons towards a  $\pi$ -bond, movement of a  $\pi$ -bond towards a carbocation or movement of a lone pair towards a carbocation.

The next example shows how an electron-deficient carbocation is stabilized by an adjacent atom that bears a lone pair. Again, note that the arrow starts at an electron pair. The resulting resonance structure is a very important one since, unlike the original (left) structure, all atoms have their octets.

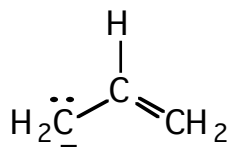


In the vinyl cation, the positive charge cannot be delocalized by the  $\pi$ -electrons because the empty p-orbital on C is orthogonal to the electrons in the  $\pi$ -bond.

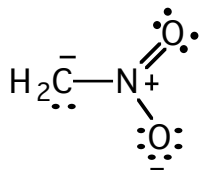


Armed with these examples, you should be able to discover all of the resonance structures of the following molecules. Enjoy.

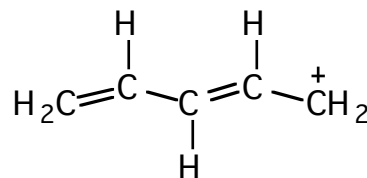
The allyl anion:



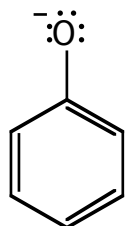
The conj. base of nitromethane:



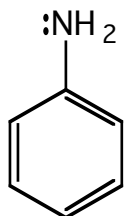
The pentadienyl cation:



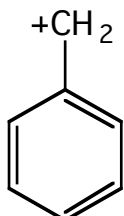
The phenoxide anion



Aniline:

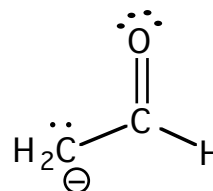


The benzyl cation:

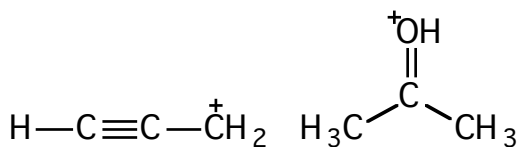


Conj. base of

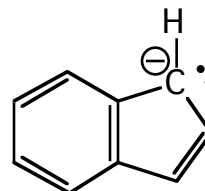
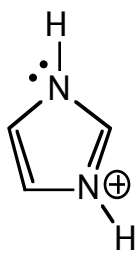
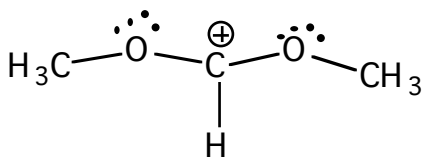
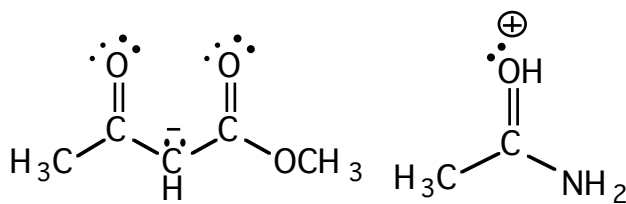
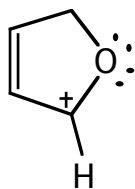
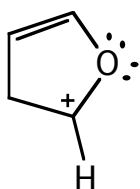
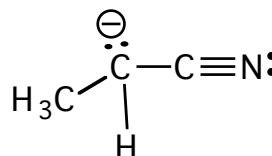
(Conj. base of phenol)



The propargyl cation:

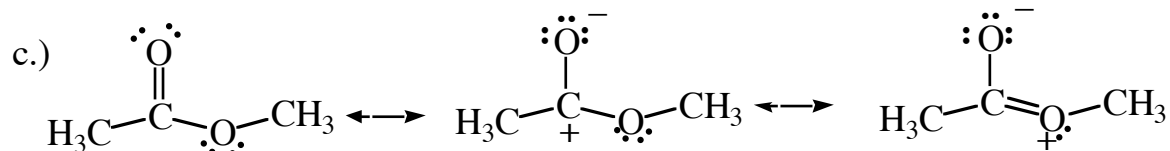
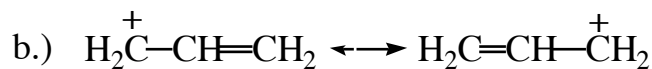
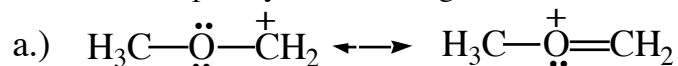


Conj. base of propionitrile:



### Question

In each of the following, judge which of the resonance structures are more or less important contributors than the others. Explain your reasoning.



### Answer

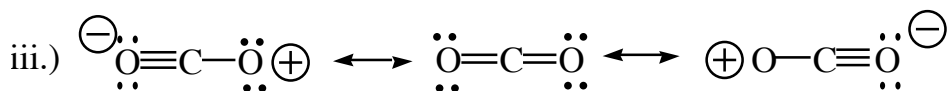
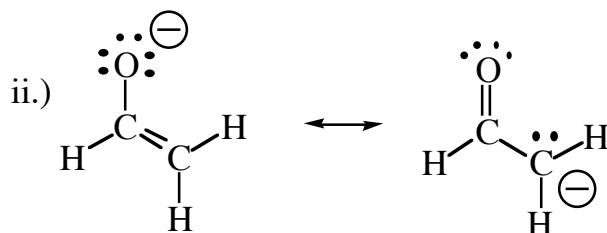
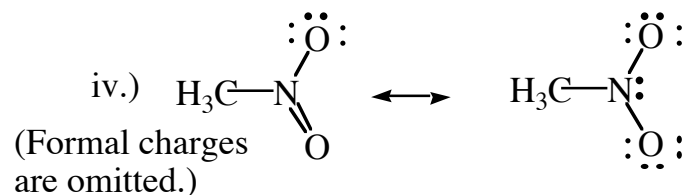
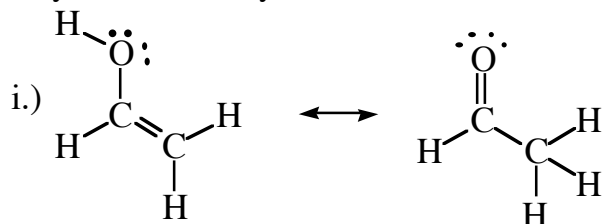
a) The left-hand structure has an electron deficient carbon where the right-hand structure has complete octets for all atoms. This makes the right-hand structure more favourable, even though it puts a positive charge on oxygen.

b) These structures are degenerate (equal). Please note that these are DIFFERENT RESONANCE STRUCTURES NONETHELESS. These structures imply that the charge is delocalized over 2 carbon atoms, and indeed, this kind of carbocation (called an allylic carbocation) is resonance stabilized.

c) The first structure is most favoured. It has no electron-deficient atoms, nor does it have any charge separations (as the third structure has). The third structure is favoured over the second (middle) structure for the reasons outlined in (a) above.

### Question Six

For the following sets of resonance structures, check to see that all structures are valid according to the rules set out in your text. If they are not valid, indicate why not.



### Answer

i.) These are not resonance structures because a proton is shifting its position. This violates Rule 2. The process shown does take place but it represents a **chemical equilibrium** between two distinct chemical species. This is known as a **tautomerism**; in this case an enol-keto tautomerism.

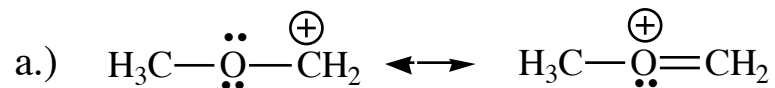
ii.) This looks a lot like (i.) but without the proton shift. These are valid resonance structures for a species known as the enolate anion, very important in carbonyl chemistry.

iii.) If you count the electrons around the O atom with the negative formal charge you will note that it comes to 10, 2 more than an octet. This is not valid for 2nd row elements (see Rule 4).

iv.) The structure on the left has two more electrons than the one on the right. This violates Rule 3. If you worked the formal charges out you probably noticed that these two species have different overall charges. That's not allowed either.

**Question Four (four marks)** Explain your reasoning.

For the two species shown, evaluate the resonance structures and determine:



i.) which atom bears most of the charge in the species?

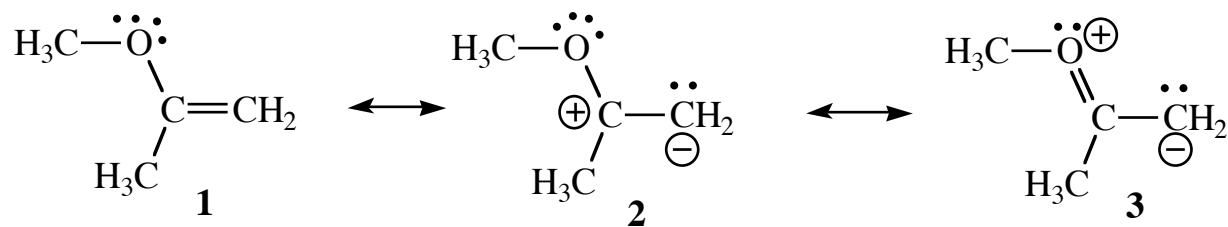
ii.) does the oxygen-CH<sub>2</sub> bond length correspond more closely to a single or a double bond?

**Answer**

The right hand resonance structure contributes more to the character of this species since all atoms have their octets. As a result, the O atom clearly bears most of the charge and the O-CH<sub>2</sub> bond length will be closer to double bond length.

**Question Five (six marks)**

The following are all valid resonance structures for methyl isopropenyl ether. **All non-bonding electrons are shown.**



a) Rank them in decreasing order of importance, i.e. which structure contributes most to the character of this molecule, etc. Explain your reasoning.

b) What do these structures imply about the C=C bond length?

**Answer**

Structure 1 is best since it is uncharged and all atoms have their octets. Structure 3 is next best because all atoms have octets. Structure 2 is the least important since carbon is electron deficient.

These structures imply that there is a small amount of double bond character in the carbon-carbon bond making it a little shorter.

**Question One**

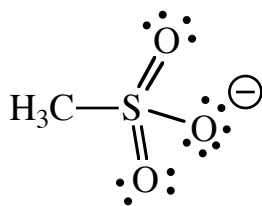
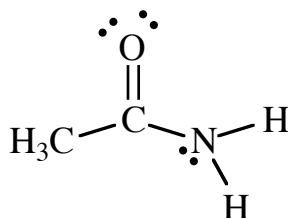
Give all reasonable resonance structures of the following.

a) [H<sub>3</sub>COCHOCH<sub>3</sub>]<sup>+</sup>

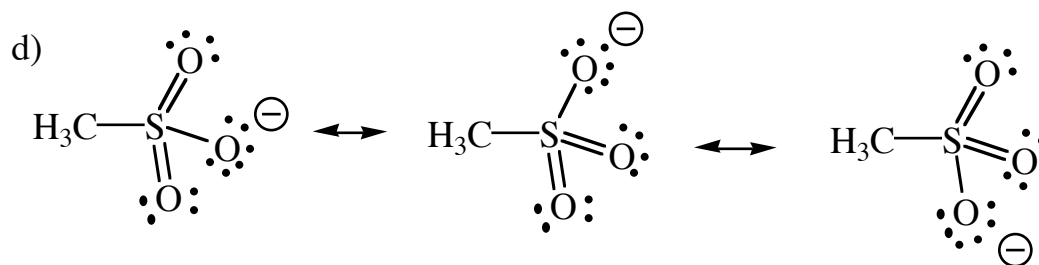
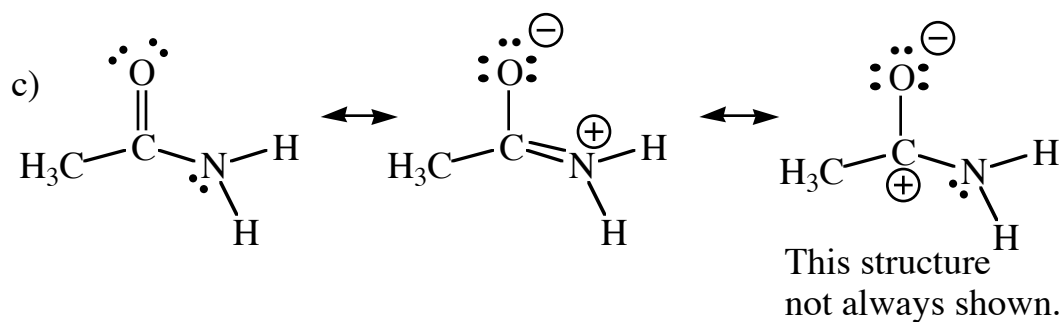
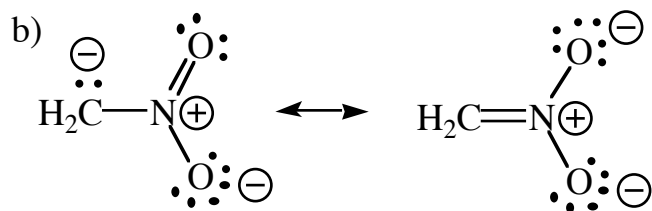
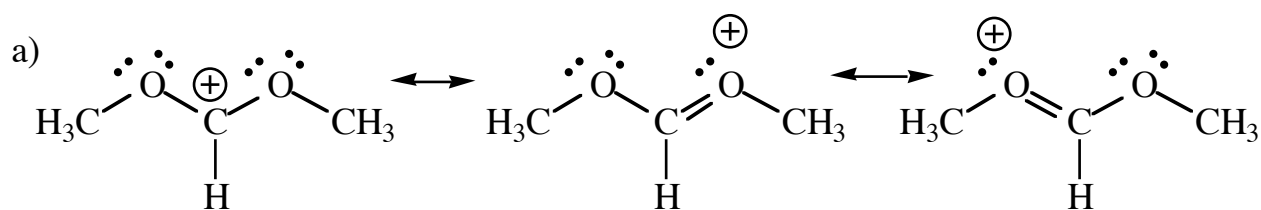
b) [CH<sub>2</sub>NO<sub>2</sub>]<sup>-</sup>

c)

d)

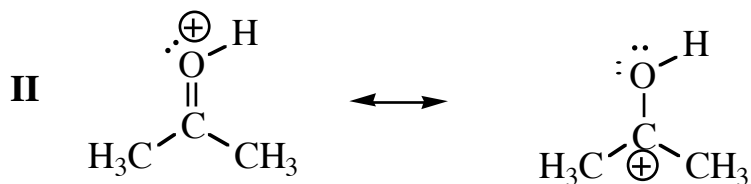
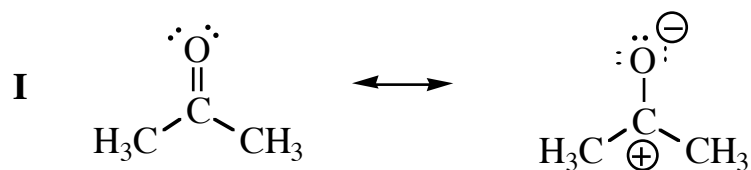


### Answer



### Question

The following pairs of resonance structures describe the molecule acetone (I) and protonated acetone (II).



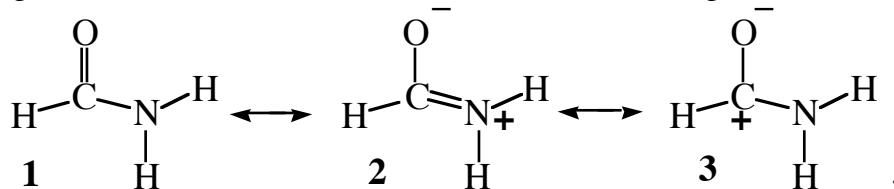
Examine the two pairs of resonance structures. Which of these two species (I or II) has the most electrophilic character? (In both cases, the right-hand structure has a carbocationic carbon that is capable of acting as an electrophile. You must keep in mind the rules for determining the "favourability" of certain resonance structures over others and also that molecules are hybrids (sort of weighted averages) of their resonance structures.)

### Answer

This is an important point but a tricky thing to perceive. We are comparing two species (I and II) each of which is represented by two resonance structures. In each pair of resonance structures, the left-hand structure is the one that contributes the most character (because all atoms have full octets). Comparing the right-hand structures, we note that for I we have a destabilizing charge separation and an electron deficient carbon while for II we have no charge separation, only the electron-deficient carbon. As a result, the right-hand structure of II contributes more to the character of II than the right-hand structure of I contributes to the character of I. Since the right-hand structure in each case is the one which has the electrophilic carbocation character, this means that II will be more electrophilic than I.

### Question (5 marks)

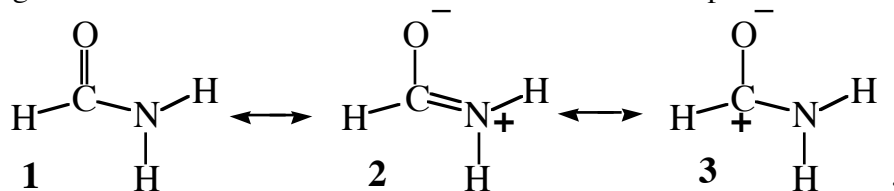
a.) Rank the following resonance structures for this molecule in order of importance and state your reasoning.



b.) The molecule above can act as a Brønsted base. Will it accept a proton on the O atom or the N atom? Explain your reasoning.

### Question Seven (5 marks)

a.) Rank the following resonance structures for this molecule in order of importance and state your reasoning.



b.) The molecule above can act as a Brønsted base. Will it accept a proton on the O atom or the N atom? Explain your reasoning.

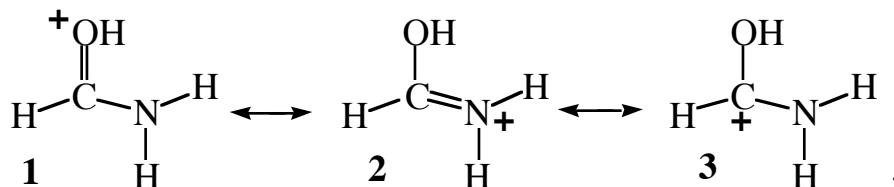
### Answer

a) The structure **1** is the most important contributor to the character of formamide. All atoms have octets and (unlike the latter two structures) there are no charge separations (see Rule 5).

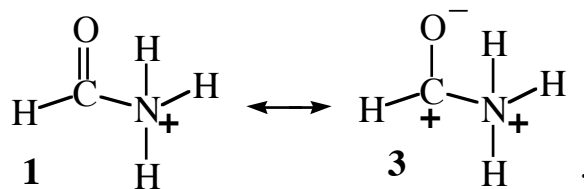
The next most important contributor is the middle structure. While it has a charge separation (making less important than the first structure) all atoms have complete octets (unlike the third structure). Another way of noting this is that it has one more bond than the last structure (three lines as opposed to only two). See Rule 4.

The least important contributor is the last structure. It has a charge separation and also has an electron deficient carbon atom (having only six electrons; the carbon bearing the positive charge).

b) To figure this out, you might have looked at the resonance structures of the conjugate acid of this compound that result from protonation on the O atom vs. protonation on the N atom. For O atom protonation there are three possible structures:



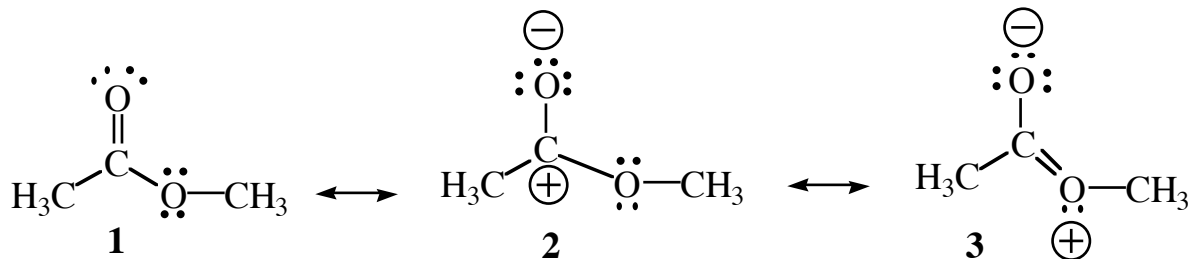
For N atom protonation there are only two:



As a result, it is clear that the conjugate acid which results from protonation on the O atom is more resonance stabilized than that resulting from N protonation. This will make the O atom effectively more basic. Note, that this is opposite to the case described in question 4, where resonance factors are not involved.

### Question One (6 marks)

- What functional group does this molecule contain?
- Rank the following resonance structures in order of importance by saying which one contributes most to the character of this molecule, and which contributes least. **Explain your reasoning.**

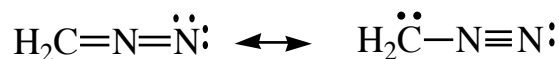


### Answer

- It is an ester.
- Structure 1 is best since there are no charges and no electron deficient atoms. Structure 2 is the smallest contributor since it has an electron deficient C atom and a charge separation. Structure 3 is intermediate between 1 and 2 because it has a charge separation but more bonds (no electron deficient atoms) as does 2.

### Question (6 marks)

The following resonance structures are used to describe the molecule diazomethane. It is a bright yellow, volatile, toxic, explosive and useful material.



- Indicate the presence of any formal charges on these resonance structures by placing + and/or - signs above the appropriate atoms. Show all such charges in both structures.
- What is the hybridization of the central N atom? \_\_\_\_\_
- Which resonance structure contributes more to the character of diazomethane: the one on the left or the one on the right? \_\_\_\_\_ Explain your reasoning.
- Indicate in which direction the net molecular dipole of diazomethane points by labeling one of the structures with a dipole vector.
- Where would a proton,  $\text{H}^+$ , attack this molecule: on the C atom, the central N atom or on the terminal N atom? \_\_\_\_\_

### Answer

i.)

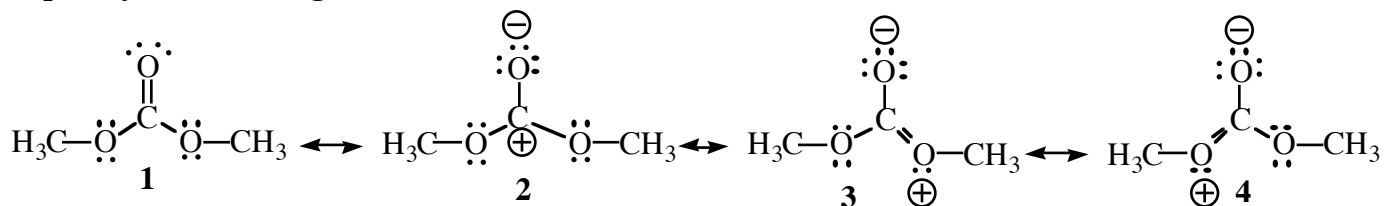


- ii) It is sp hybridized.
- iii) Both structures are the same in terms of charge and the number of bonds. The left hand structure is best, in that the negative charge is located on the more electronegative atom.
- iv) Based on which structure dominates the character of this molecule, one would draw a dipole pointing from carbon to nitrogen.
- v) Dizaomethane protonates on carbon since C- is more basic than N- (C less electronegative than N).



**Question (6 marks)**

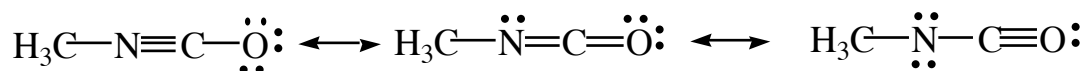
i.) Rank the following resonance structures in order of importance by saying which one contributes most to the character of this molecule, and which contributes least. Identify any degenerate (equivalent) structures. Explain your reasoning.

**Answer**

Structure **2** is the least important contributor (has fewer bonds - electron deficient carbon and bears charges). Structures **3** and **4** are degenerate (contribute equally). They have the same number of bonds as structure **1** but have charges present. Structure **1** is the most important contributor. No charges and no electron deficient atoms.

**Question (6 marks)**

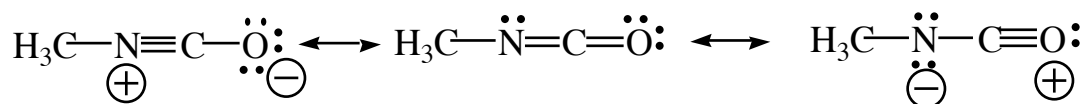
The following resonance structures are used to describe the molecule methyl isocyanate. It is the toxic gas that was at the root of the Bhopal disaster.



- Indicate the presence of any formal charges on these resonance structures by placing + and/or - signs above the appropriate atoms. Show all such charges in all structures.
  - What is the hybridization of the central C atom? \_\_\_\_\_
  - Of the two, which resonance structure contributes more to the character of methyl isocyanate: the one on the left or the one on the right? \_\_\_\_\_ Explain your reasoning.
- iv.) Indicate in which direction the net molecular dipole of methyl isocyanate points by labeling one of the structures with a dipole vector.

**Answer**

i)



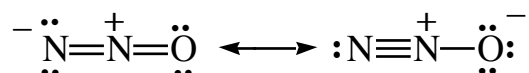
- It is sp hybridized.
- Both structures have the same number of bonds and same charges. The best structure will have the negative charge on the more electronegative atom. That would be the left hand structure.
- The dipole should point towards the O atom.

**Question**

N<sub>2</sub>O is a linear molecule in which the atoms are ordered NNO. Draw the resonance structures for this molecule and indicate which contribute more to the character of this molecule. On the basis of this, what net dipole would you expect for this molecule?

**Answer**

The two resonance structures are:



In both cases all atoms have their octets. In both cases there are two charges, one of them being a positive charge on the central N atom. The difference, then, is the placement of the negative charge. This charge will prefer to sit on the more electronegative oxygen atom, therefore the right-hand structure will be the major resonance structure and the net molecular dipole will point toward the O atom. Other valid resonance structures can be written but they involve large charge separations or incomplete octet atoms.