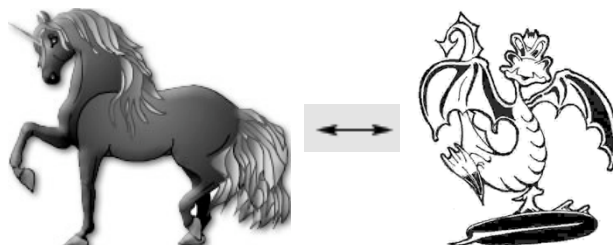


Resonance



What Is Resonance?

Example

•Carbon monoxide $:\text{C}=\ddot{\text{O}}:$ versus $-\text{:C}\equiv\text{O:}+$

Which accurately represents the molecular structure?

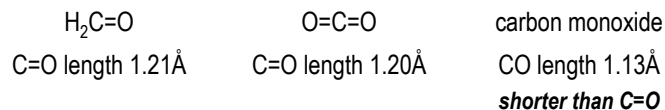
- Open octet on carbon vs. formal charges - both decrease stability
- Double bond (longer) versus triple bond (shorter)

What Is Resonance?

The Lewis structure of CO

Double bond or triple bond?

- Laboratory analysis of C-O bond lengths



- Empirical observations of dipole moment rule out triple bond.

Conclusion

- The Lewis structure that accurately represents CO is...

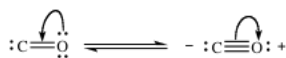


Empirical observation: Actual structure is somewhere in between double and triple bond.

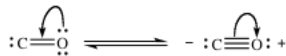
What Is Resonance?

The Lewis structure of CO

Perhaps an equilibrium between two structures that differ in electron distribution?



Curved Arrows

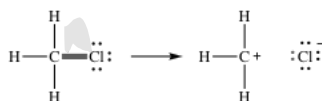


A curved arrow...

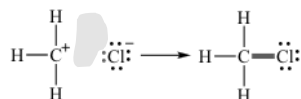
- Indicates electron redistribution
- Starts at electron source; points to electron destination:

Electron source  Electron destination

- When arrow starts at bond, bond is broken:



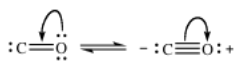
- When arrow points to atom or space between atoms, bond is formed:



What Is Resonance?

The Lewis structure of CO

Perhaps CO is equilibrium between two structures that differ in electron distribution?

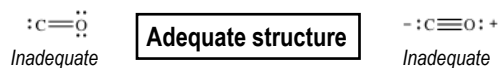


- Equilibrium ruled out by empirical evidence.

What Is Resonance?

The Lewis structure of CO

Empirical CO structure is *intermediate between* the Lewis structures:



What is this “between” structure?

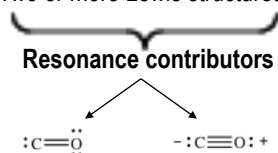
- Each inadequate structure has some, but not all, actual features of CO
- CO cannot be adequately represented by a single Lewis structure
- Therefore “blend” or “average” inadequate structures → composite structure

What Is Resonance?

A definition

Resonance

- Molecule cannot be adequately represented by just one Lewis structure
- Two or more Lewis structures must be used.



How Do We Indicate a Molecule Has Resonance?



Resonance

Accurate depiction of CO



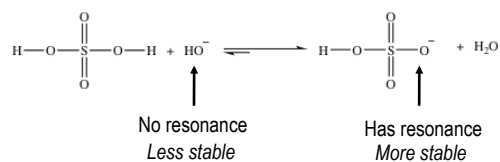
Equilibrium

Not accurate for CO

Why Is Resonance Important?

- *Common occurrence* with Chem 14C atoms: C, N, O, F, Cl, Br, I, S, P
- Resonance delocalization *increases stability*: electrons (charge) spread over larger volume \uparrow stability
- Resonance *influences molecular structure*: causes planarity

Resonance importance example: An acid-base reaction

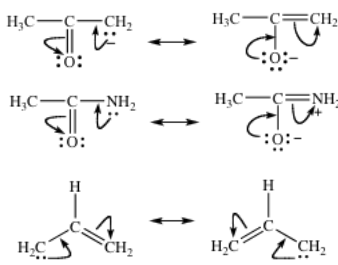


$$K_{eq} > 1$$

H₂SO₄ stronger acid than H₂O

Drawing Resonance Contributors

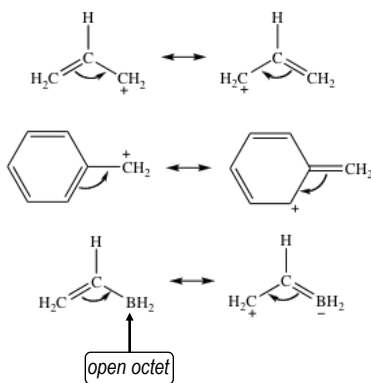
Key: recognize electron pair shift patterns



What is electron pair shift pattern?

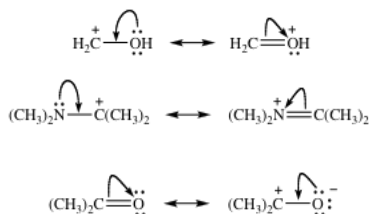
Note: Not necessary to draw for both sides of

Drawing Resonance Contributors



What is electron pair shift pattern?

Drawing Resonance Contributors



What is electron pair shift pattern?

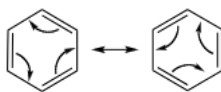
Most common resonance patterns

- Lone pair/pi bond trade places
- Pi bond/open octet trade places
- Lone pair + open octet switches with pi bond

Drawing Resonance Contributors

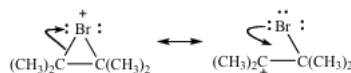
Less common electron pair shift patterns

Pi bonds switch:



Common for benzene rings

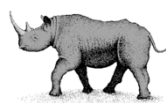
Single bond and lone pair switch:



Only rarely important

Which Resonance Contributor Represents Reality?

Once upon a study break...



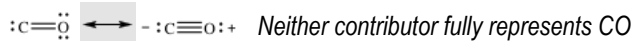
Fantasy creatures

Neither fully represents reality

Real creature

A unicorn-dragon hybrid?

The carbon monoxide case:

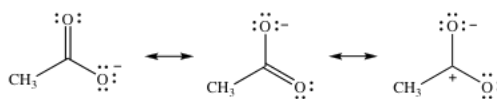


Resonance hybrid: a weighted average or blend of resonance contributors; the *most accurate representation* of the electronic structure of a molecule.

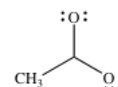
Drawing the Resonance Hybrid

Example: Draw the resonance hybrid for acetate ion, CH_3CO_2^- .

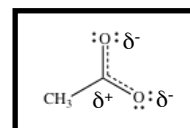
1. Draw contributors



2. Draw the features (sigma and pi bonds, lone pairs, formal charges) that are the same for all contributors



3. Add features that are not the same for all contributors



Resonance hybrid

Do All Contributors Have Equal Importance?

Is a rhinoceros more unicorn or more dragon?

\uparrow contributor "stability" = \uparrow resemblance to reality = \uparrow contribution to hybrid

Therefore we need contributor preference ("stability") rules:

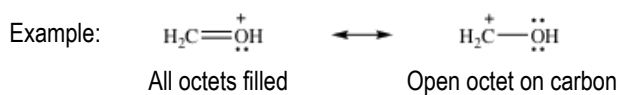
\uparrow number and/or magnitude of rules violations

= \downarrow importance of individual contributor

= \downarrow contribution to resonance hybrid

Resonance Contributor Preference Rules

Rule #1: The most important contributor has the maximum number of atoms with full valence shells.



In some cases it may not be possible for all atoms to have full valence shells.

Rule #1 is more influential than all the other preference rules.

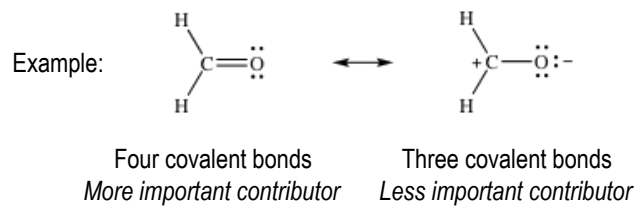
Rules #2-6 have no particular order of preference.

→ "One Ring to rule them all, One Ring to find them,
One Ring to bring them all and in the darkness bind them"



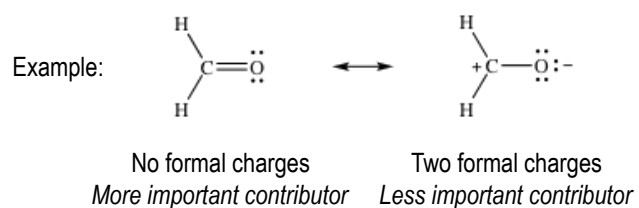
Resonance Contributor Preference Rules

Rule #2: The most significant contributor has the maximum number of covalent bonds.



Resonance Contributor Preference Rules

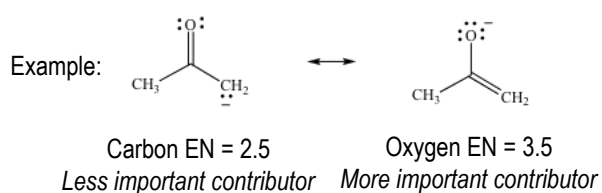
Rule #3: The most significant contributor has the least number of formal charges.



Resonance Contributor Preference Rules

Rule #4: If a contributor must have formal charge(s), the most important contributors has these charges on the atom(s) that can best accommodate them.

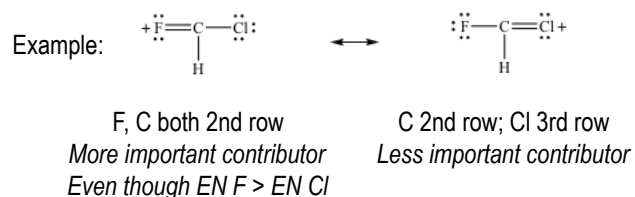
- Negative formal charges best on atoms of high electronegativity
- Positive formal charges best on atoms of low electronegativity



Resonance Contributor Preference Rules

Rule #5: Resonance interaction (i.e., pi bond) is strongest between atoms in the same row of the periodic table.

- Usually CNOF
- Usually outweighs electronegativity considerations (rule #4)



13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
B 10.81 Boron	C 12.01 Carbon	N 14.01 Nitrogen	O 16.00 Oxygen	F 18.99 Fluorine	Ne 20.18 Neon
Al 26.98 Aluminum	Si 28.09 Silicon	P 30.97 Phosphorus	S 32.07 Sulfur	Cl 35.45 Chlorine	Ar 39.95 Argon
Ga 69.72 Gallium	Ge 72.61 Germanium	As 74.92 Arsenic	Se 78.96 Selenium	Br 79.90 Bromine	Kr 83.80 Krypton
In 114.82 Indium	Sn 118.71 Tin	Sb 121.76 Antimony	Te 127.60 Tellurium	I 126.90 Iodine	Xe 131.29 Xenon

Resonance Contributor Preference Rules

Rule #6: Other factors (carbocation stability, etc.) that we will encounter later.

Violations to the resonance contributor preference rules exist, but are uncommon.