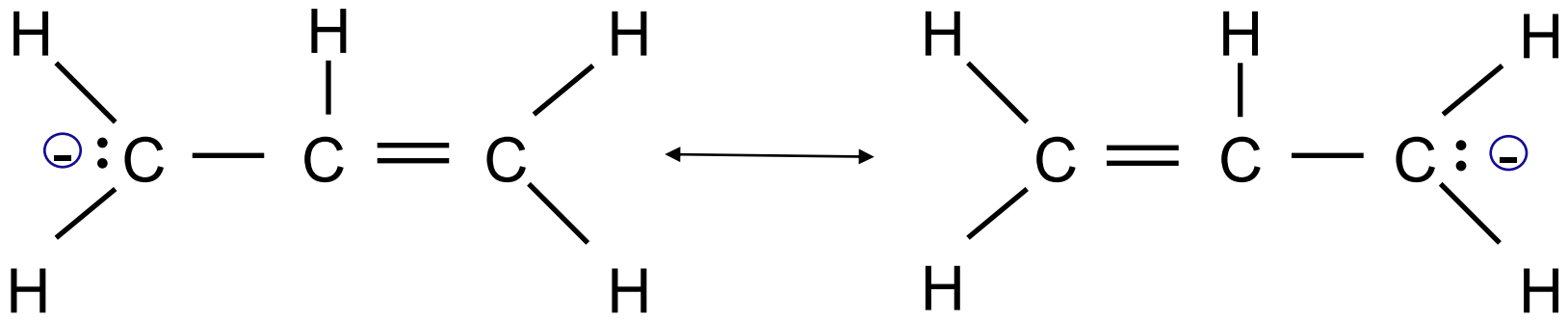
Structures

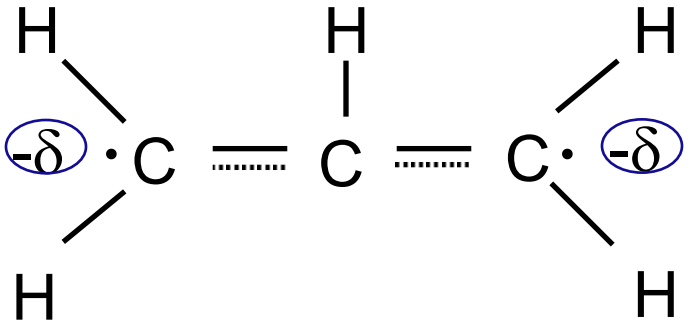
Reading: Gray: (2-14)
OGN: (3.6)

Resonance Structures

two structural possibilities for $[C_3H_5]^-$:

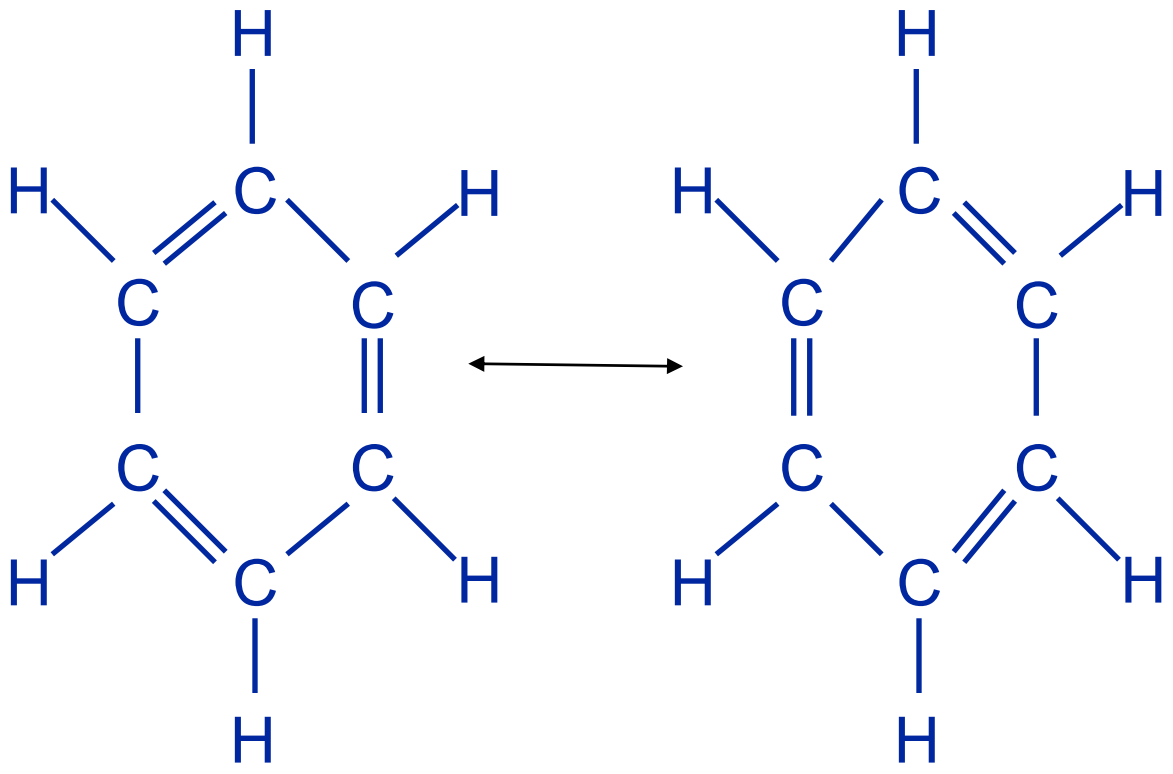


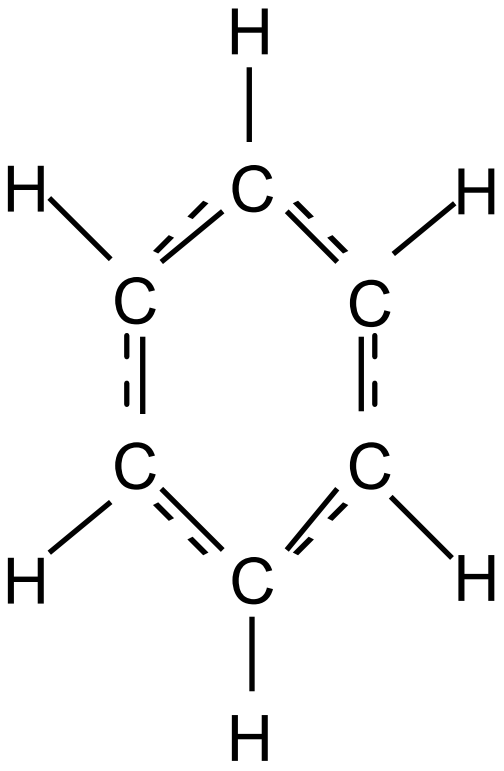
however, the actual molecule is neither of the two structures:



Resonance Structures: Another Example

Two structural possibilities for benzene:

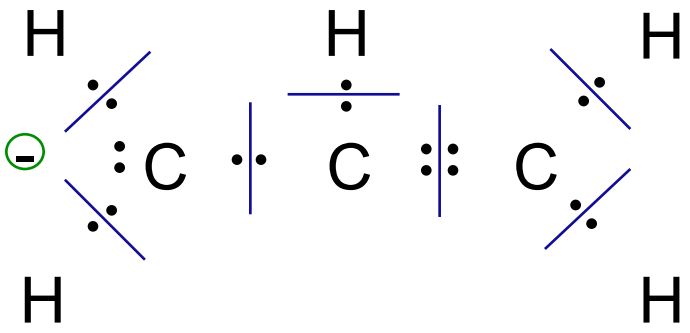




Each C - C bond can be thought of as a 1.5-electron bond in the actual structure

Formal Charge

Formal Charge: the difference between the number of valence shell electrons for an element and the number of electrons surrounding it in a molecule (including half of the bond electrons and all the free electrons)



Example:

The leftmost carbon has 3 bonds with 2 electrons each, plus 2 free electrons; so it has 5 electrons surrounding it. The formal charge equals the valence electrons minus surrounding electrons:

4 - 5 = –1 = Formal Charge

“Reasonable” Resonance Structures

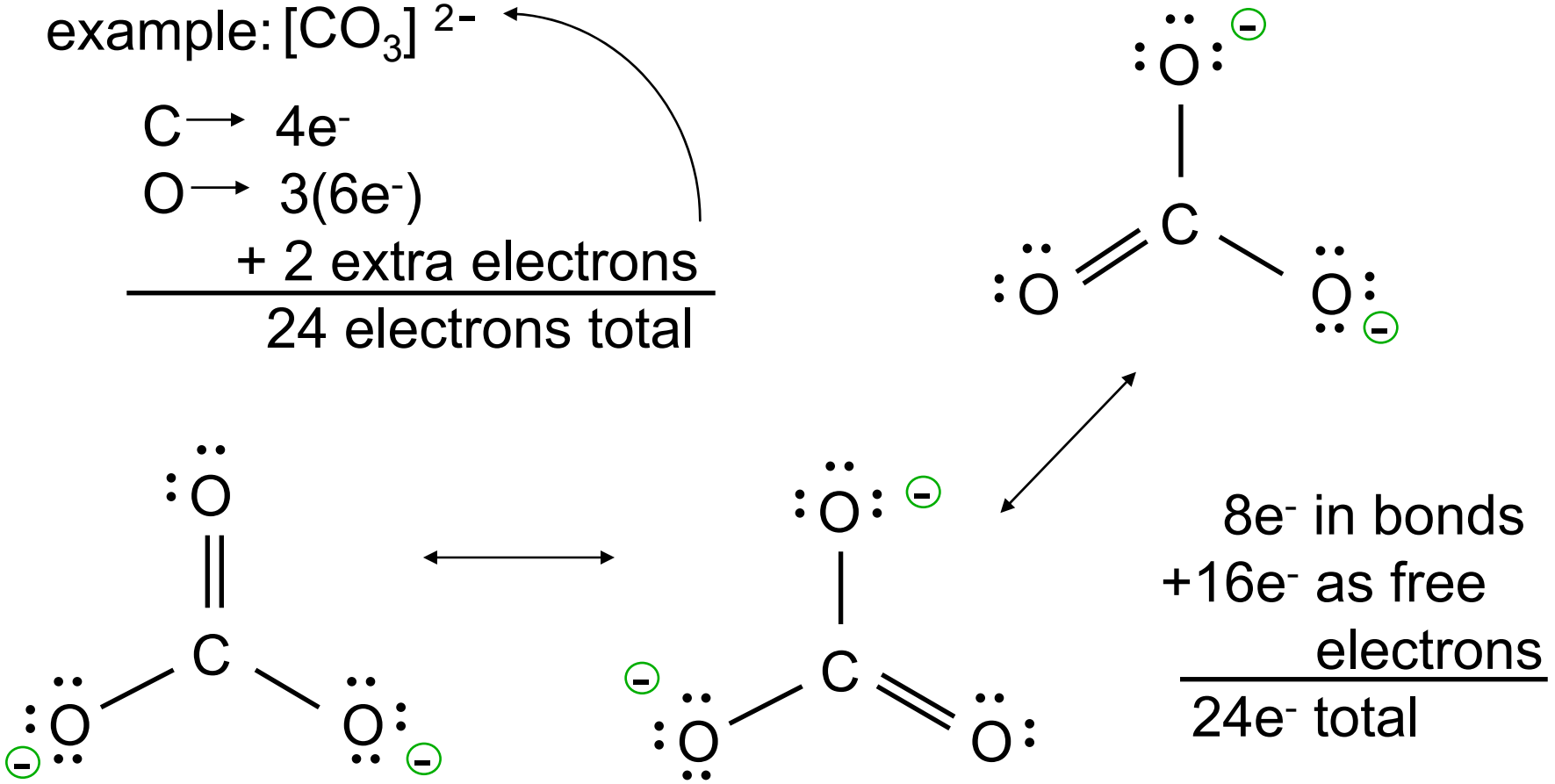
1. Form octets if possible
2. Maximize bonding
3. Distribute formal charges in a reasonable way
   -minimize if possible
   -more negative on more electronegative atoms
   -avoid same sign on neighboring atoms

Drawing Resonance Structures

Count the number of electrons available, and devise a reasonable structure having that many electrons

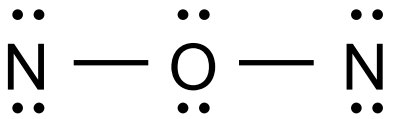
example: $[CO_3]^{2-}$

C → 4e⁻
O → 3(6e⁻)
+ 2 extra electrons
24 electrons total

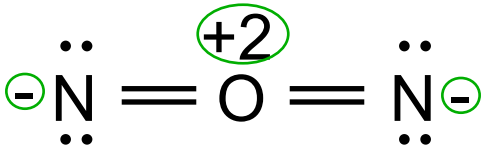


Resonance Structures of N_2O

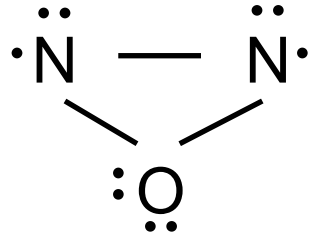
$N_2O \rightarrow 2(5e^-) + 6e^- = \mathbf{16e^-}$



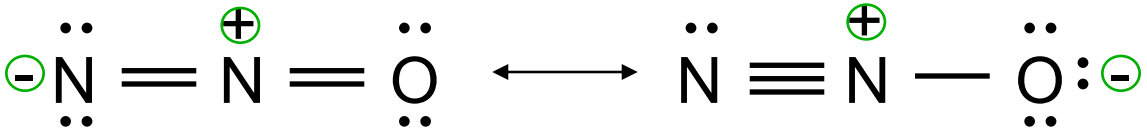
this structure won't work: no octets on N's



nor this one: high formal charges



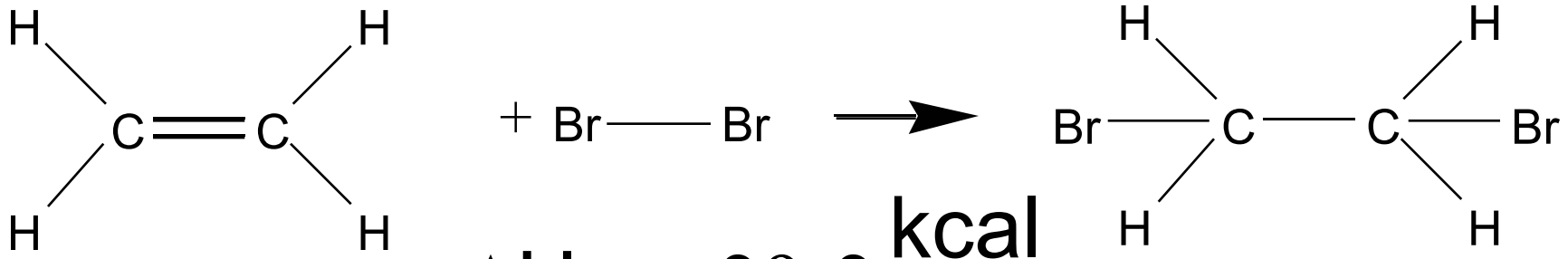
nor this one: such configurations are destabilized by "ring strain"



best structures possible

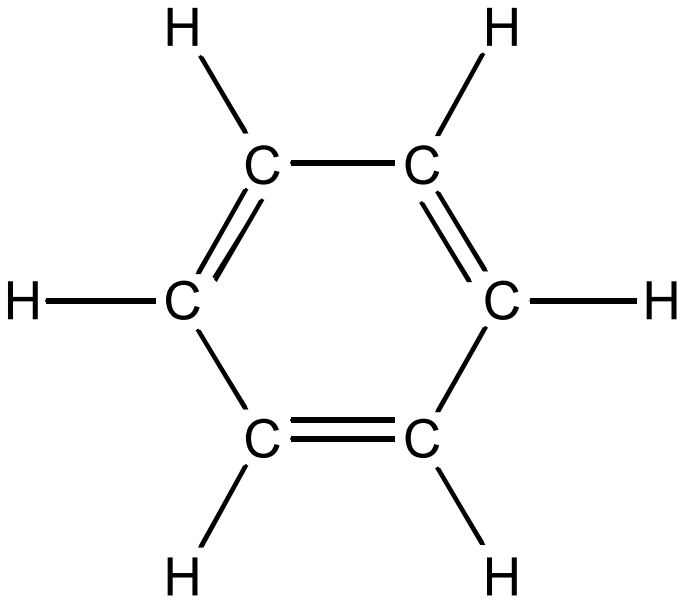
Benzene:

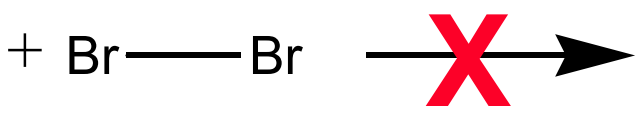
- **Much more stable and much less reactive than 3 isolated double bonds**



$$\Delta H = -29.2 \frac{\text{kcal}}{\text{mol}}$$

but...

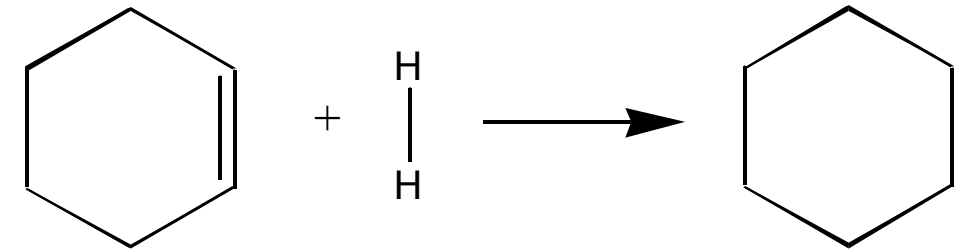




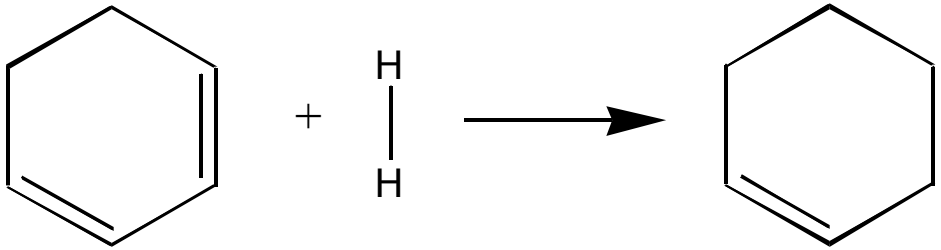
No Reaction

$$\Delta H = +2 \frac{\text{kcal}}{\text{mol}}$$

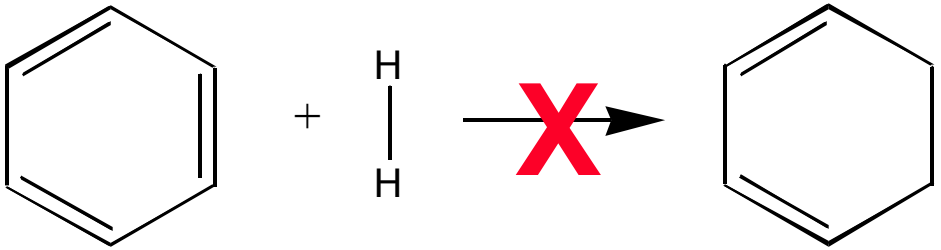
Benzene's "Resonance Stabilization"



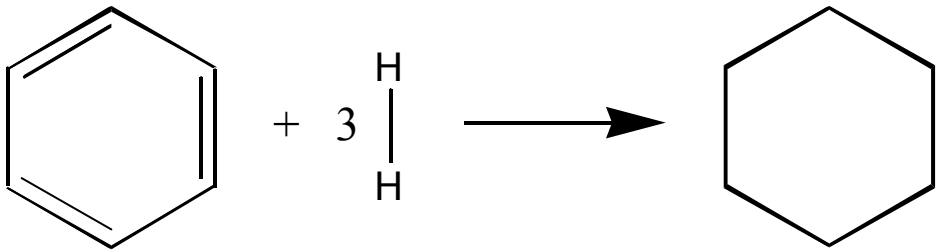
$$\Delta H = -28.4 \ \frac{\text{kcal}}{\text{mol}}$$



$$\Delta H = -26.5 \ \frac{\text{kcal}}{\text{mol}}$$



$$\Delta H = +5.6 \ \frac{\text{kcal}}{\text{mol}}$$



$$\Delta H = -49.3 \ \frac{\text{kcal}}{\text{mol}}$$

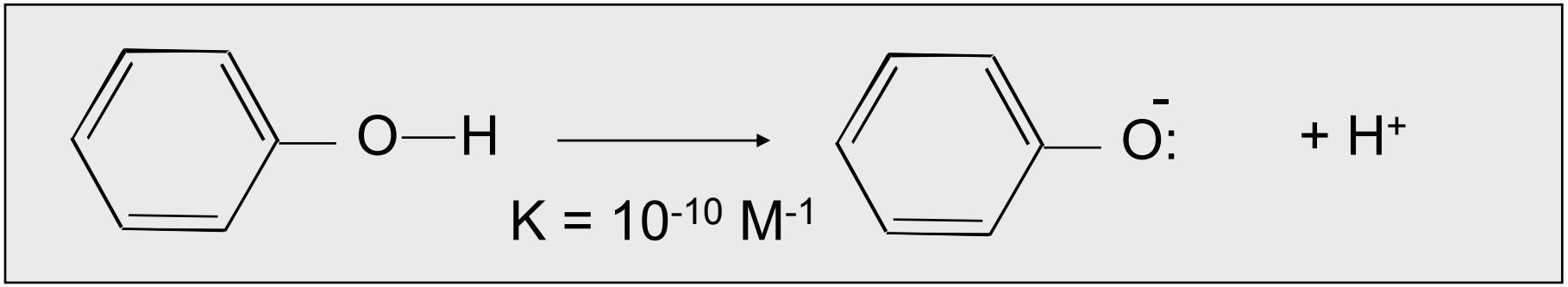
More Resonance Stability

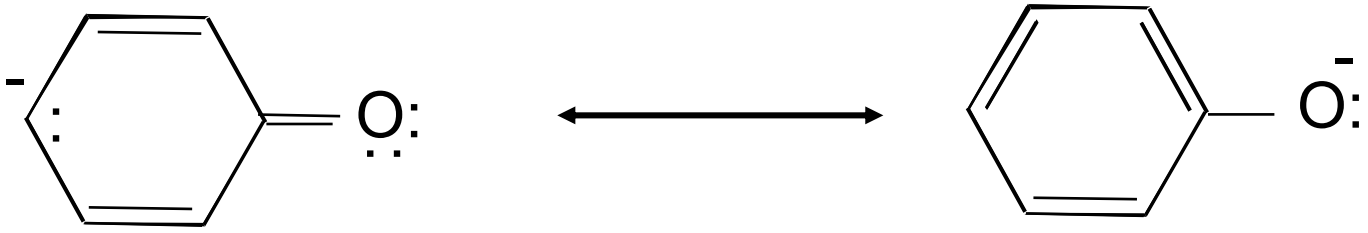
Propanol

$H_3C\text{-}CH_2\text{-}CH_2\text{-}OH \longrightarrow H_3C\text{-}CH_2\text{-}CH_2\text{-}O^- + H^+$

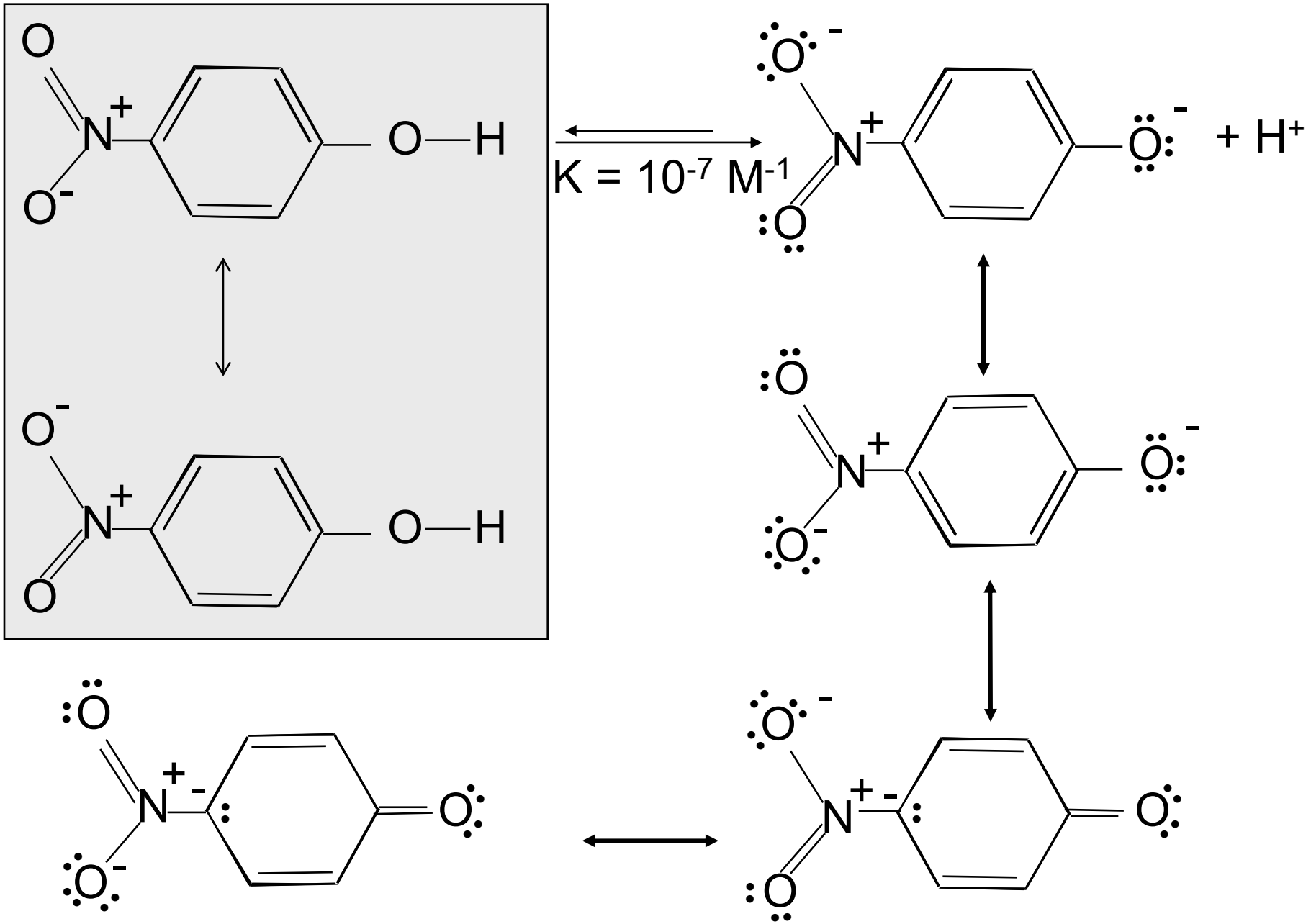
$K \approx 10^{-15}\ M^{-1}$

Phenol

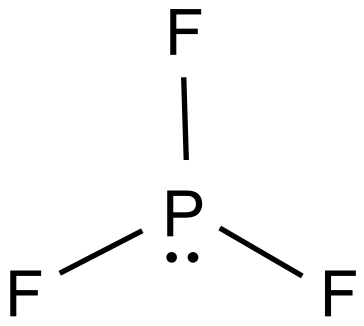




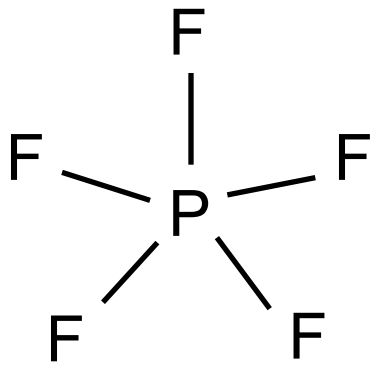
More Resonance Stability



Expanded Octets



PF_3



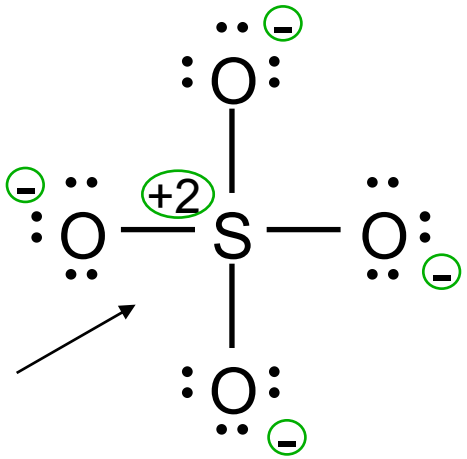
PF_5

- Elements whose valence electrons aren't constrained to be in the s and p orbitals (they move to the d orbital in this example) don't necessarily have to have eight electrons around them

Bond Order

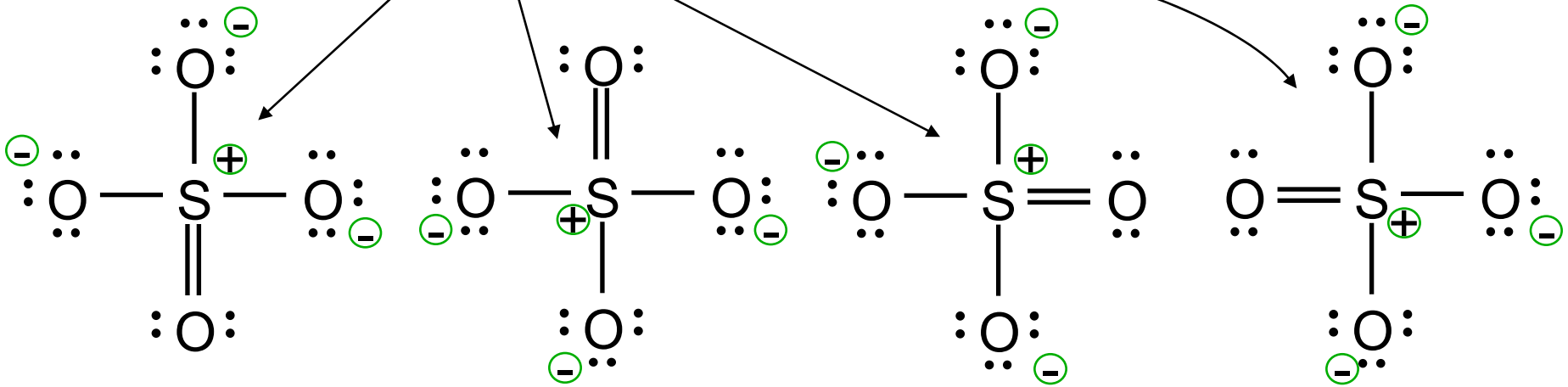
Bond Order: the average number of bonds connecting an element to the central atom

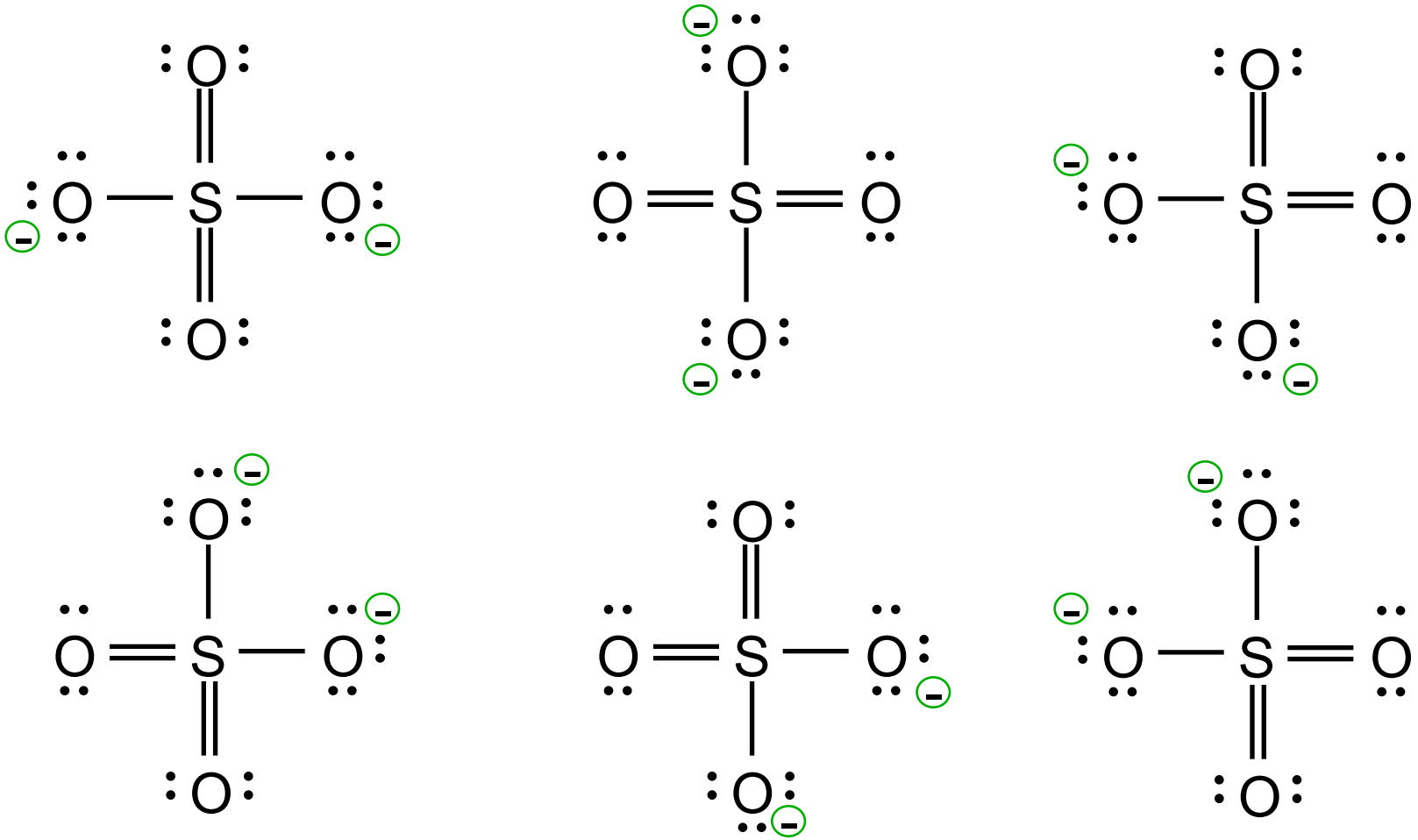
Example: Resonance structures of SO_4^{2-} and their bond orders:



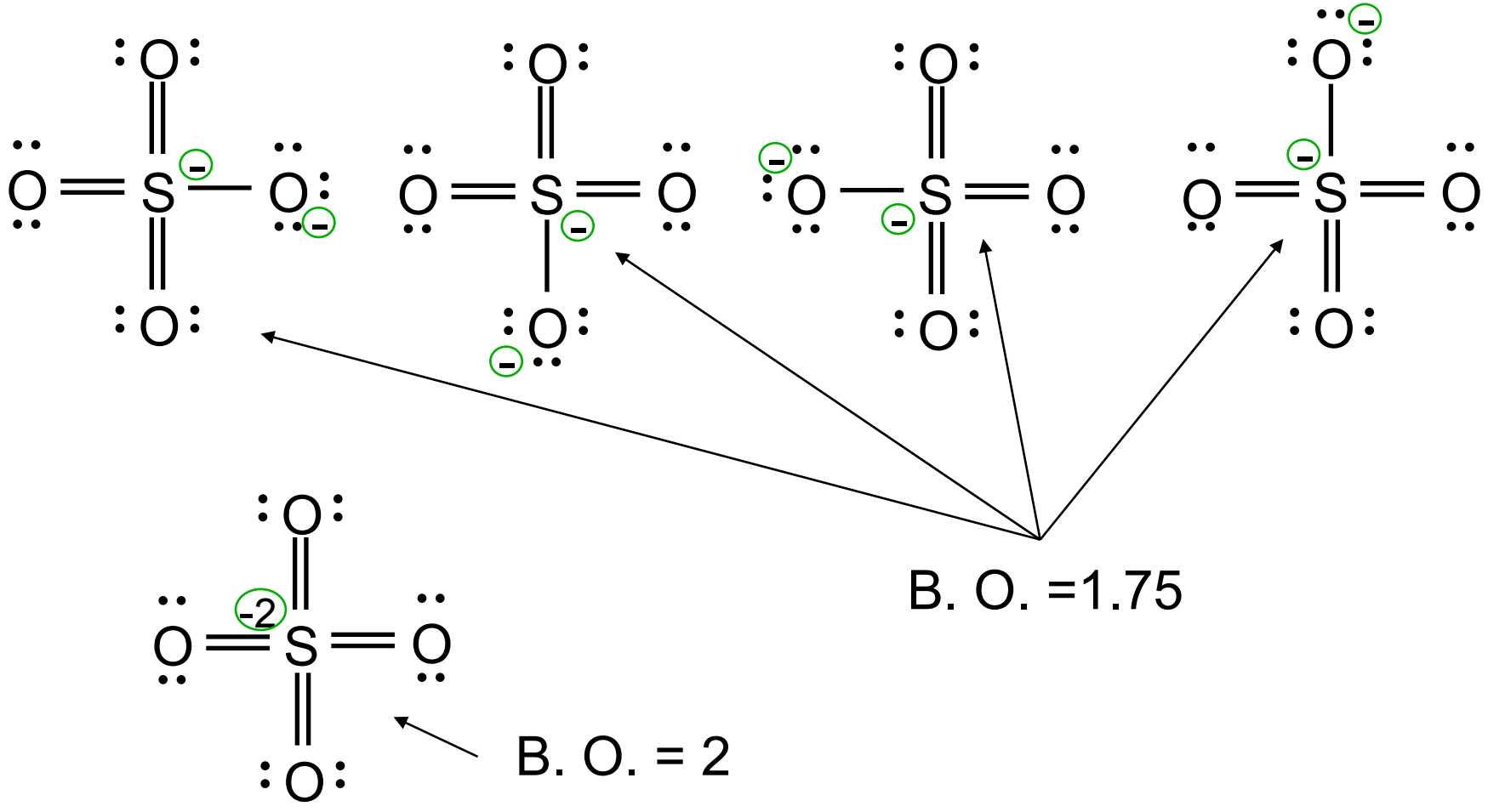
B. O. =1.0

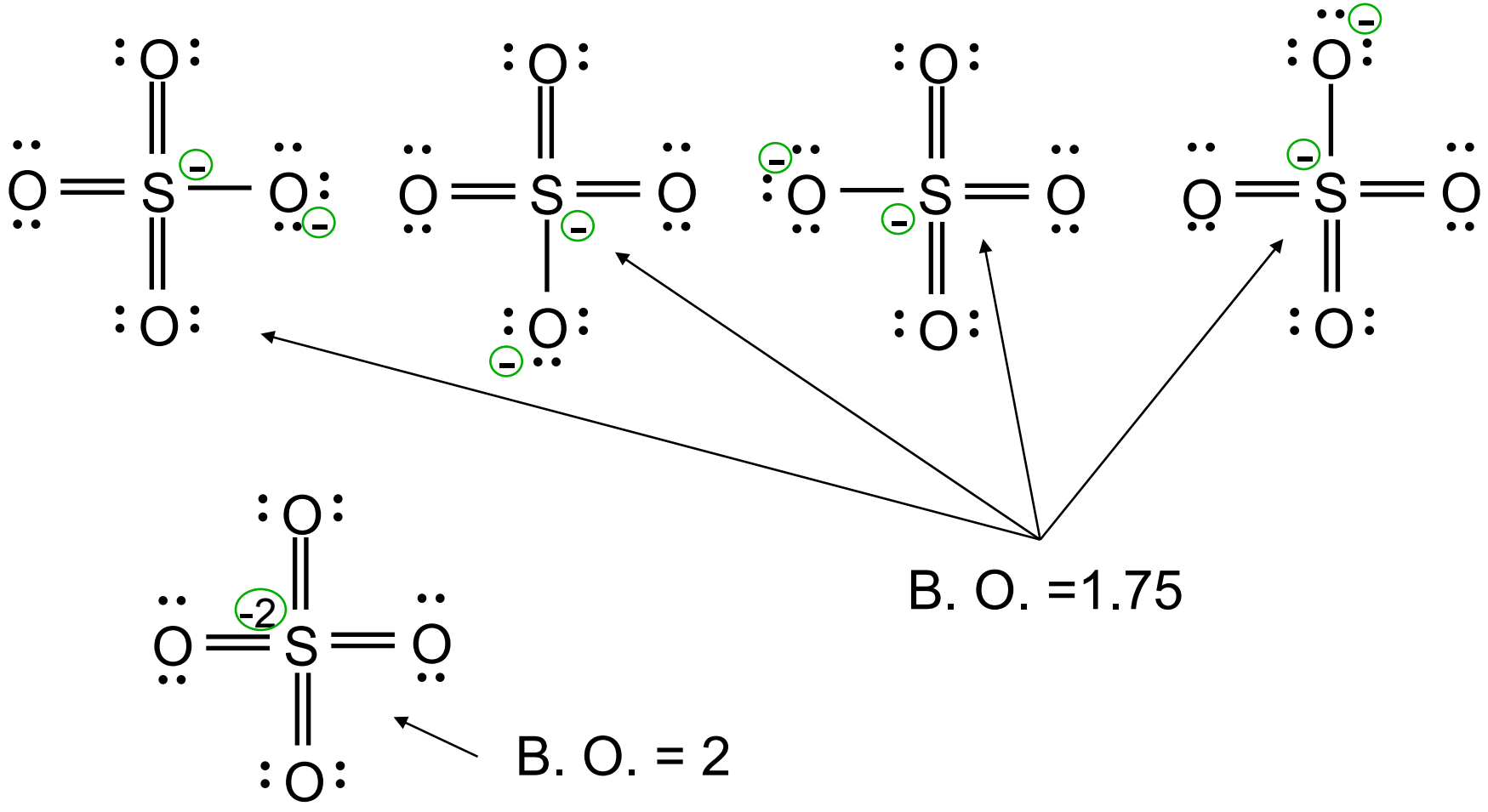
B. O. =1.25





Bond Order (B.O.) = 1.5


B. O. =1.75
B. O. = 2



The actual bond order of the molecule is **1.8**

Acidity of Oxoacids, -X-O-H

	pK		pK
$HClO_4$	-7	H_3AsO_4	2.30
$HClO_3$	-3	HNO_2	3.34
H_2SO_4	-2	H_2CO_3	6.37
HNO_3	-1.3	HSO_3^-	6.91
HIO_3	0.80	$H_2AsO_4^-$	7.03
H_2SO_3	1.81	$H_2PO_4^-$	7.21
HSO_4^-	1.92	HClO	7.53
$HClO_2$	1.96	HCO_3^-	10.32
H_3PO_4	2.12	$HAsO_4^{2-}$	11.53
		HPO_4^{2-}	12.67

How can we understand the trends in acidity of oxoacids?

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		HPO_4^{2-}	12.67

As X becomes more electronegative
X withdraws electron density from O;
Hence makes O less basic (more acidic)
$H_3AsO_4 < H_3PO_4 < HNO_3$ (up a column)

Acidity of Oxoacids, -X-O-H

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$HClO_4$	-7
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H_2SO_4	-2
HNO_3	-1.3
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H_2SO_3	1.81
HSO_4^-	1.92
$HClO_2$	1.96
H_3PO_4	2.12

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$HClO_2$	1.96
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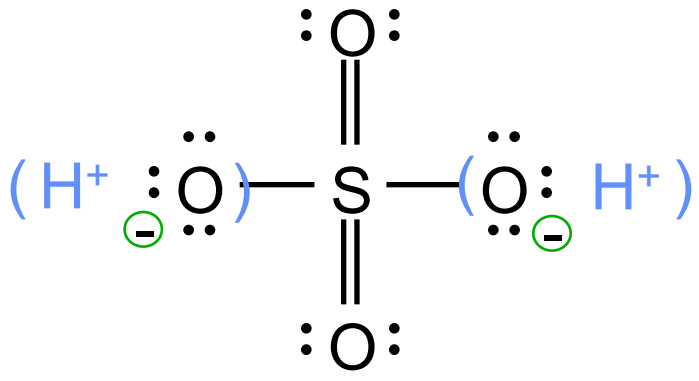
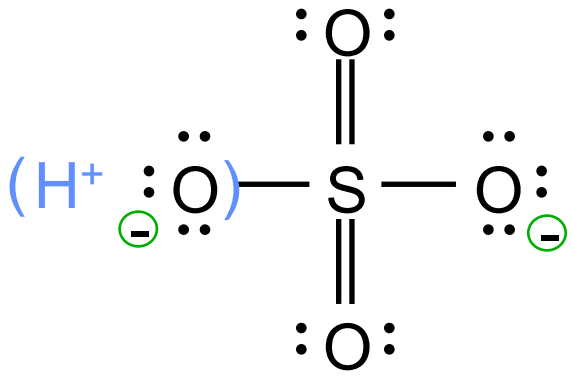
As X becomes more electronegative
X withdraws electron density from O;
Hence makes O less basic (more acidic)
$H_3AsO_4 < H_3PO_4 < HNO_3$
$H_2CO_3 < HNO_3 < HClO_4$ (across a row)

Acidity of Oxoacids

H_2SO_4, H_3PO_4, HNO_3, H_3AsO_4
All have a general formula:

$XO_n(OH)_m$





$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$

H_2SO_4 : m=2 n=2

HSO_4^- : m=1 n=3

Acidity of Oxoacids

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$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	H_2SO_4 : m=2 n=2 K = 10^3
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	HSO_4^- : m=1 n=3 K = 10^{-2}

$$K_n/K_{n-1} = 10^{(-4.5\pm0.5)}$$

After each dissociation, increased negative charge lessens tendency to lose next H^+

Acidity of Oxoacids, -X-O-H

	pK		pK
$HClO_4$	-7	H_3AsO_4	2.30
$HClO_3$	-3	HNO_2	3.34
H_2SO_4	-2	H_2CO_3	6.37
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Acidity of Oxoacids

H_2SO_4, H_3PO_4, HNO_3, H_3AsO_4, etc.

General formula: $XO_n(OH)_m \rightleftharpoons XO_{n+1}(OH)_{m-1} + H^+$

$HClO_4 \rightleftharpoons H^+ + HClO_4^-$	$HClO_4$:	m=1 n=3
$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	H_2SO_4 :	m=2 n=2
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	H_2CO_3 :	m=2 n=1

K larger when n larger

n	K_1	Acid Strength
3	Very, very large	Very strong
2	10^2	Strong
1	10^{-2} - 10^{-3}	Medium
0	$10^{-7.5}$ - $10^{-9.5}$	Weak

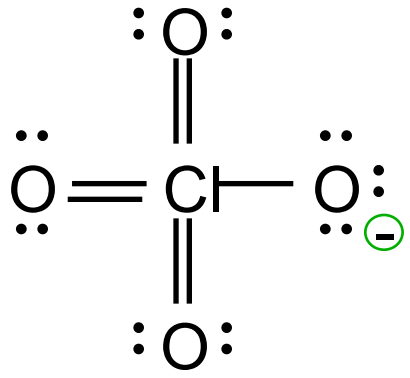
Acidity of Oxoacids

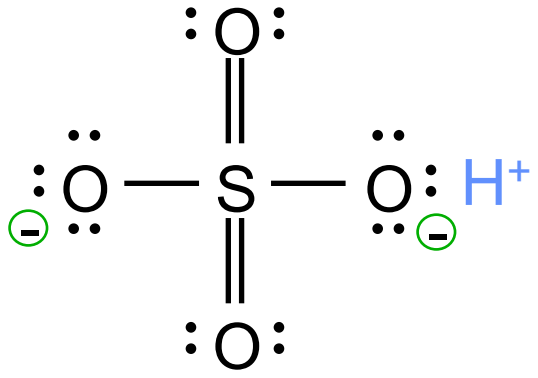
H_2SO_4, H_3PO_4, HNO_3, H_3AsO_4, etc.

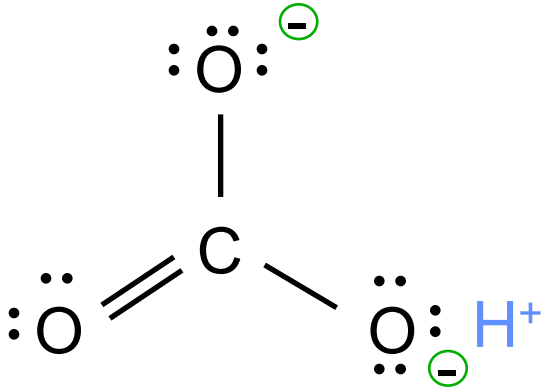
General formula: $XO_n(OH)_m \rightleftharpoons XO_{n+1}(OH)_{m-1} + H^+$

$HClO_4 \rightleftharpoons H^+ + HClO_4^-$	$HClO_4$: m=1 n=3
$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	H_2SO_4 : m=2 n=2
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	H_2CO_3 : m=2 n=1

K larger when n larger







Res. Structures: (4 +...) (3 +...) (2)

Acidity of Oxoacids

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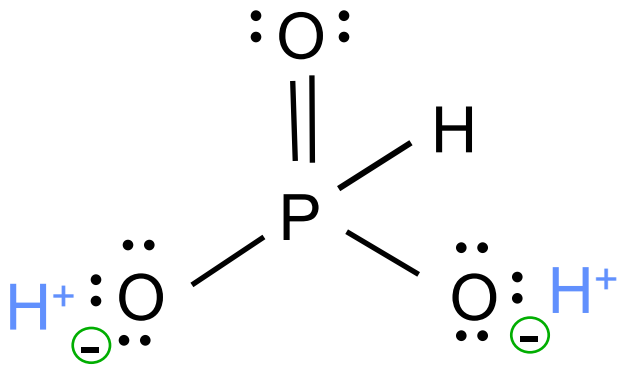
			K
$HClO_4 \rightleftharpoons H^+ + ClO_4^-$	$HClO_4$:	m=1 n=3	10^7
$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	H_2SO_4:	m=2 n=2	10^3
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	H_2CO_3:	m=2 n=1	$10^{-3.5}$
$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^-$	H_3PO_3:	m=3 n=0	10^{-2} !

H_3PO_3 is *not* $P(OH)_3$
K = 10^{-2} suggests n=1

In fact, H_3PO_3 is $HPO(OH)_2$:



END

Structures

Reading: Gray: (2-14)
OGN: (3.6)