1.7
Structural Formulas of Organic Molecules

Constitution

The order in which the atoms of a molecule are connected is called its *constitution* or *connectivity*.

The constitution of a molecule must be determined in order to write a Lewis structure.

Table 1.4 How to Write Lewis Structures

Step 1:

The molecular formula and the connectivity are determined by experiment.

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Example:

Methyl nitrite has the molecular formula CH_3NO_2. All hydrogens are bonded to carbon, and the order of atomic connections is CONO.

Table 1.4 How to Write Lewis Structures

Step 2:

Count the number of valence electrons. For a neutral molecule this is equal to the number of valence electrons of the constituent atoms.

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Example (CH_3NO_2):

Each hydrogen contributes 1 valence electron. Each carbon contributes 4, nitrogen 5, and each oxygen 6 for a total of 24.

Table 1.4 How to Write Lewis Structures

Step 3:

Connect the atoms by a covalent bond represented by a dash.

Table 1.4 How to Write Lewis Structures

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Example:

Methyl nitrite has the partial structure:

Table 1.4 How to Write Lewis Structures

Step 4:

Subtract the number of electrons in bonds from the total number of valence electrons.

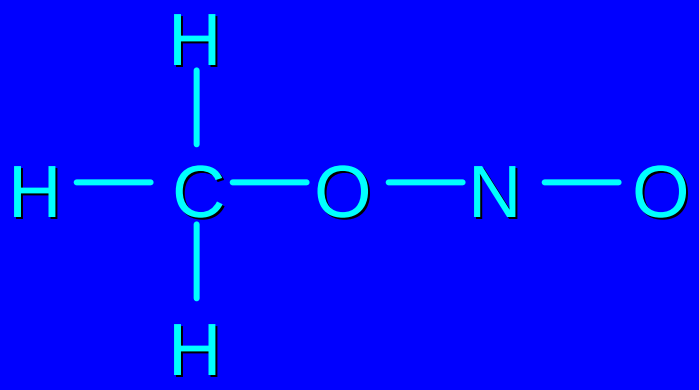

Table 1.4 How to Write Lewis Structures

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Subtract the number of electrons in bonds from the total number of valence electrons.

Example:

24 valence electrons – 12 electrons in bonds. Therefore, 12 more electrons to assign.

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Step 5:

Add electrons in pairs so that as many atoms as possible have 8 electrons. Start with the most electronegative atom.

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Example:

The remaining 12 electrons in methyl nitrite are added as 6 pairs.

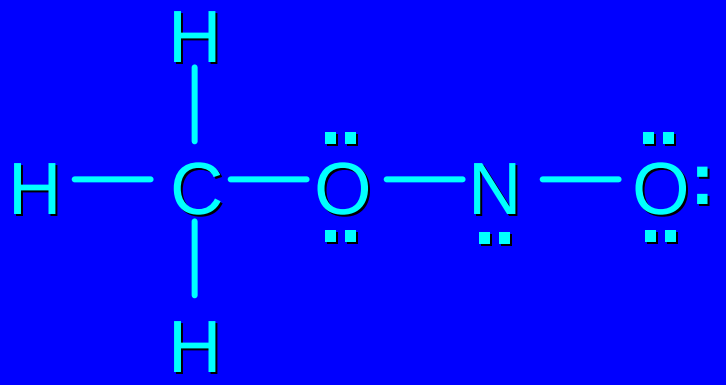

Table 1.4 How to Write Lewis Structures

Step 6:

If an atom lacks an octet, use electron pairs on an adjacent atom to form a double or triple bond.

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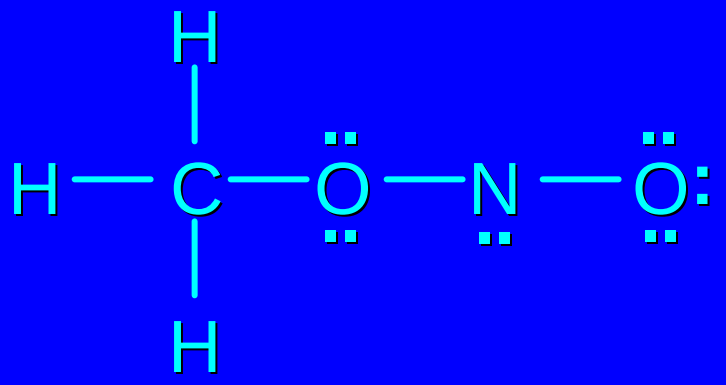

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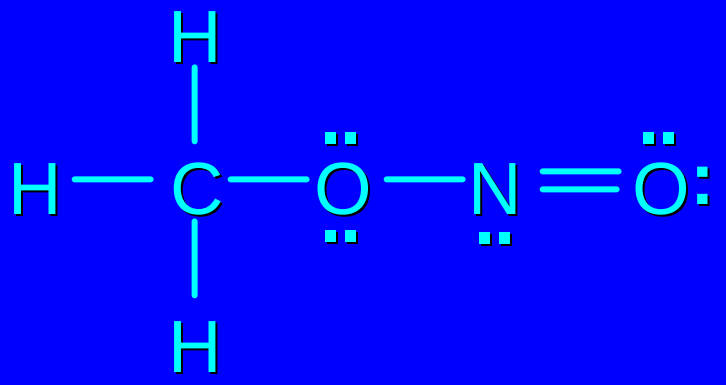


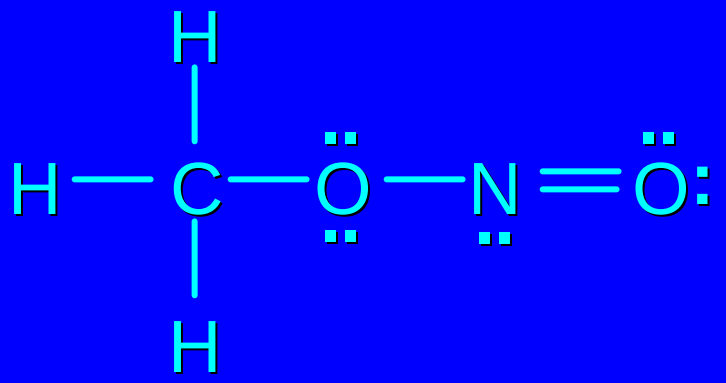
Table 1.4 How to Write Lewis Structures

Step 7:

Calculate formal charges.

Example:

None of the atoms possess a formal charge in this Lewis structure.



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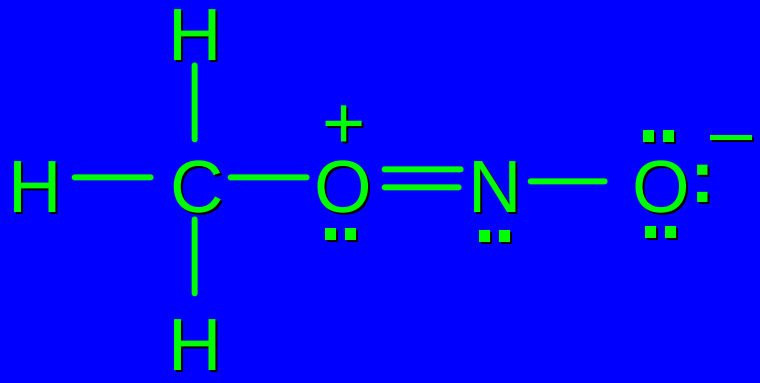
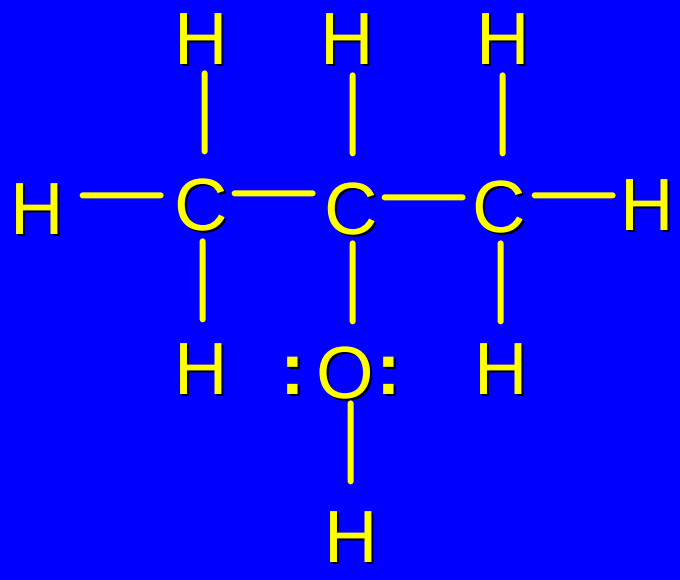
This structure has formal charges; is less stable Lewis structure.



Condensed structural formulas

Lewis structures in which many (or all) covalent bonds and electron pairs are omitted.



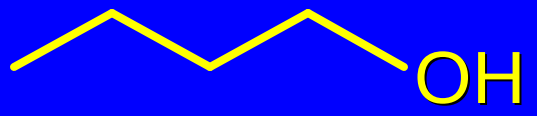
can be condensed to:

CH_3CHCH_3 or $(CH_3)_2CHOH$

OH

Bond-line formulas

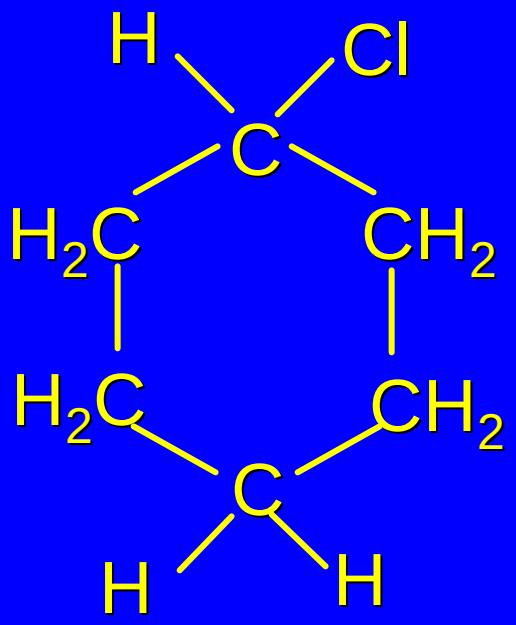
$CH_3CH_2CH_2CH_3$ is shown as 

$CH_3CH_2CH_2CH_2OH$ is shown as 

Omit atom symbols. Represent structure by showing bonds between carbons and atoms other than hydrogen.

Atoms other than carbon and hydrogen are called *heteroatoms*.

Bond-line formulas



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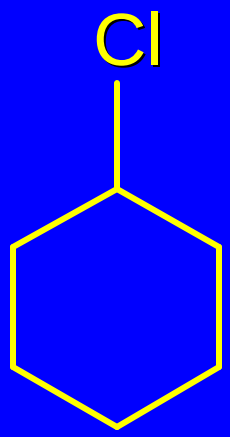

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1.8
Constitutional Isomers

Constitutional isomers

Isomers are different compounds that have the same molecular formula.

Constitutional isomers are isomers that differ in the order in which the atoms are connected.

An older term for constitutional isomers is “structural isomers.”

A Historical Note

NH_4OCN

Ammonium cyanate

H_2NCNH_2

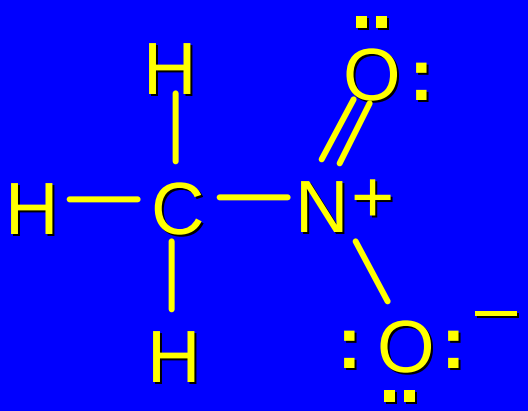
Urea

In 1823 Friedrich Wöhler discovered that when ammonium cyanate was dissolved in hot water, it was converted to urea.

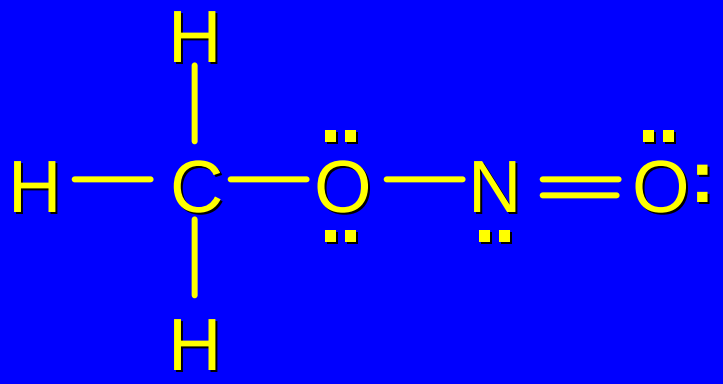
Ammonium cyanate and urea are constitutional isomers of CH_4N_2O.

Ammonium cyanate is “inorganic.” Urea is “organic.” Wöhler is credited with an important early contribution that helped overturn the theory of “vitalism.”

Examples of constitutional isomers



Nitromethane



Methyl nitrite

Both have the molecular formula CH_3NO_2 but the atoms are connected in a different order.

1.9
Resonance

Resonance

two or more Lewis structures may be written for certain compounds (or ions)

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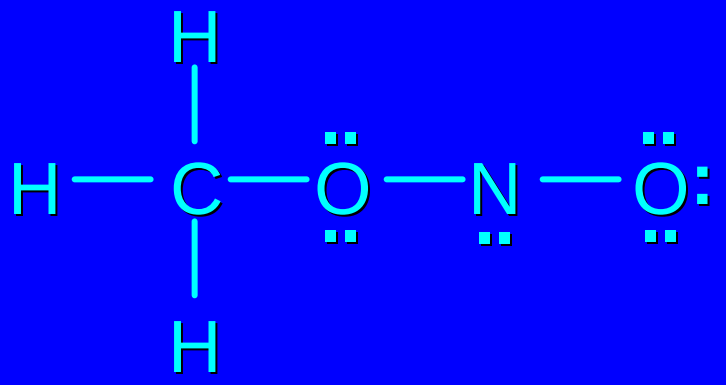

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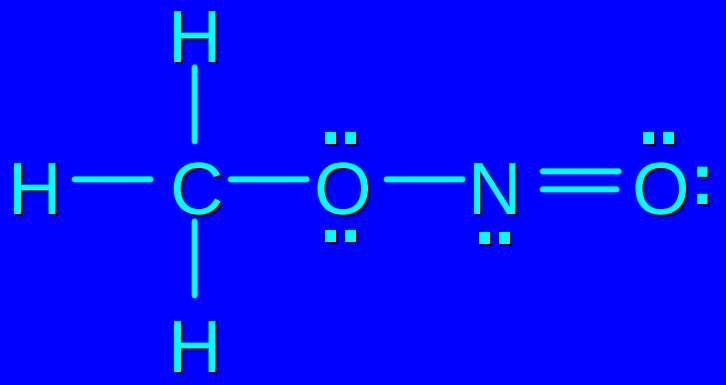

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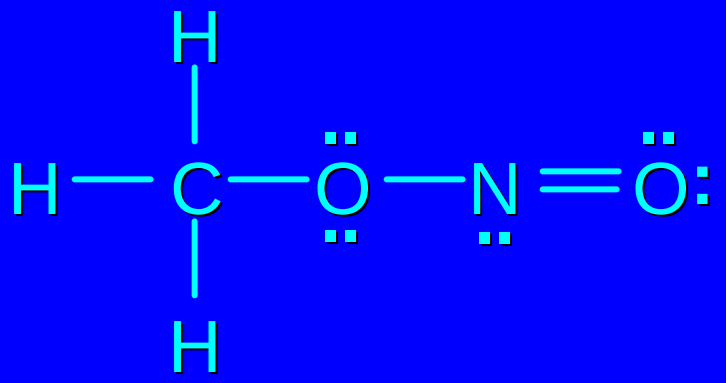

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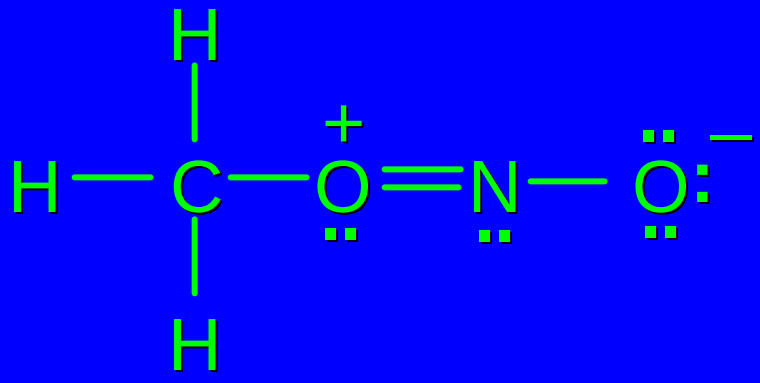
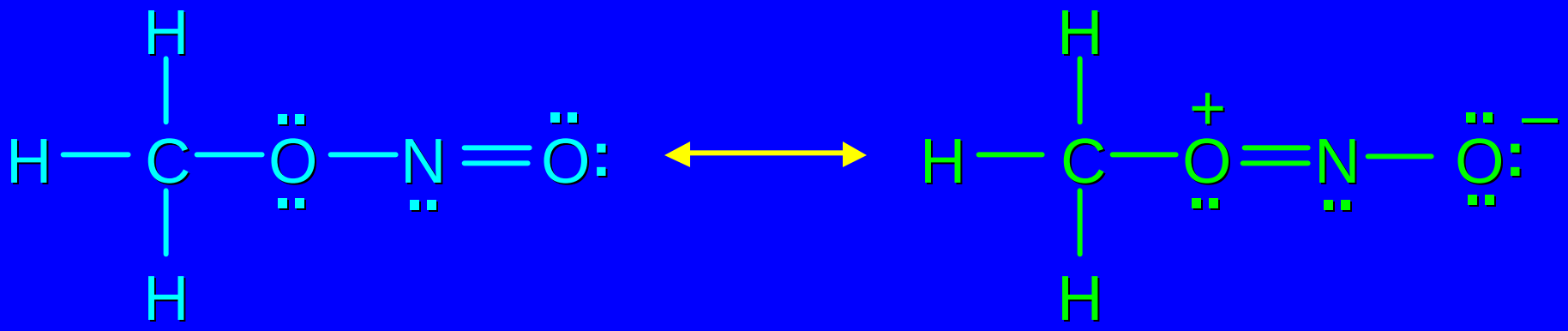


Resonance Structures of Methyl Nitrite

same atomic positions

differ in electron positions



more stable Lewis structure

less stable Lewis structure

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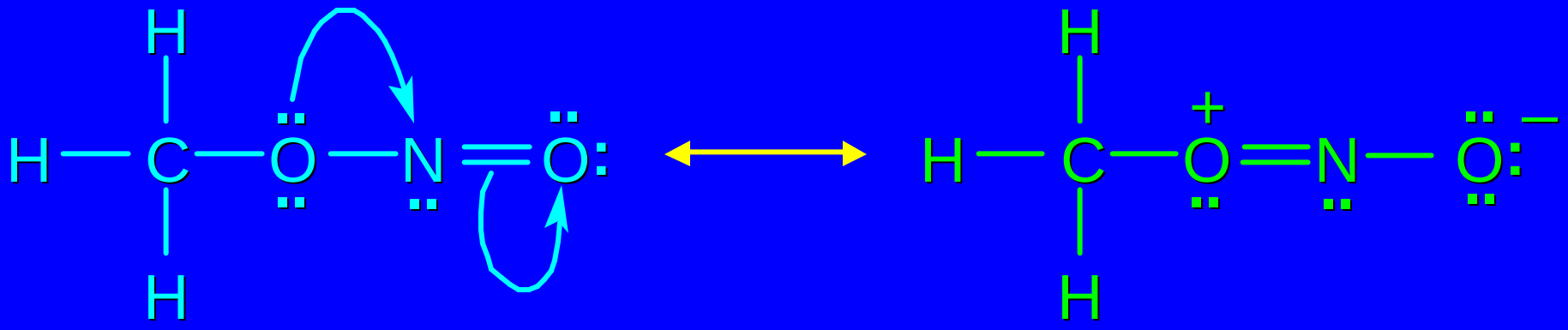


more stable Lewis structure

less stable Lewis structure

Why Write Resonance Structures?

Electrons in molecules are often delocalized between two or more atoms.

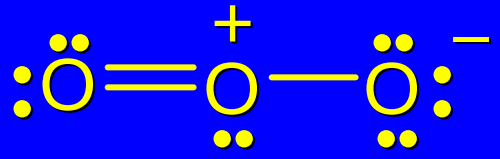
Electrons in a single Lewis structure are assigned to specific atoms-a single Lewis structure is insufficient to show electron delocalization.

Composite of resonance forms more accurately depicts electron distribution.

Example

Ozone (O_3)

Lewis structure of ozone shows one double bond and one single bond



Expect: one short bond and one long bond

Reality: bonds are of equal length (128 pm)

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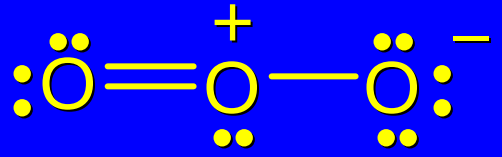

Resonance: