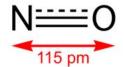
Nitric oxide

Nitric oxide (nitrogen oxide^[3] or nitrogen monoxide) is a colorless gas with the formula NO. It is one of the principal oxides of nitrogen. Nitric oxide is a free radical, i.e., it has an unpaired electron, which is sometimes denoted by a dot in its chemical formula (·N=O or ·NO). Nitric oxide is also a heteronuclear diatomic molecule, a historic class that drew

Nitric oxide





Names

IUPAC name

Nitrogen monoxide

Systematic IUPAC name

Oxidonitrogen(•)[1] (additive)

Other names

Nitric oxide

Nitrogen(II) oxide

<u>Density</u>	1.3402 g/L
Melting point	-164 °C (-263 °F; 109 K)
Boiling point	-152 °C (-242 °F; 121 K)
Solubility in water	0.0098 g / 100 ml (0 °C) 0.0056 g / 100 ml (20 °C)
Refractive index (n_D)	1.0002697
Structure	
Molecular shape	linear (point group $C_{\infty v}$)

[N]=O	
Properties	
Chemical formula	NO
Molar mass	30.006 g·mol ⁻¹
Appearance	Colourless gas

N distance in crystalline NO is 218 pm, nearly twice the N-O distance. [4]

Since the heat of formation of ·NO is endothermic, NO can be decomposed to the elements. Catalytic converters in cars exploit this reaction:

$$2 \text{ NO } \rightarrow \text{ O}_2 + \text{ N}_2.$$

When exposed to <u>oxygen</u>, nitric oxide converts into <u>nitrogen dioxide</u>:

$$2 \text{ NO} + \text{O}_2 \rightarrow 2 \text{ NO}_2.$$

This conversion has been speculated as occurring via the ONOONO intermediate.

In water, nitric oxide reacts with oxygen and water to form <u>nitrous acid</u> (HNO₂). The reaction is thought to proceed via the following <u>stoichiometry</u>:

$$4 \text{ NO} + \text{O}_2 + 2 \text{ H}_2\text{O} \rightarrow 4 \text{ HNO}_2.$$

Nitric oxide reacts with <u>fluorine</u>, <u>chlorine</u>, and <u>bromine</u> to form the nitrosyl halides, such as <u>nitrosyl chloride</u>:

$$2 \text{ NO} + \text{Cl}_2 \rightarrow 2 \text{ NOCl}.$$

With NO₂, also a radical, NO combines to form the intensely blue <u>dinitrogen</u> <u>trioxide</u>: [4]

 $NO + NO_2 = ON - NO_2$.

Organic chemistry

The addition of a nitric oxide <u>moiety</u> to another molecule is often referred to as <u>nitrosylation</u>. Nitric oxide reacts with <u>acetone</u> and an <u>alkoxide</u> to a <u>diazeniumdiolate</u> or <u>nitrosohydroxylamine</u> and <u>methyl acetate</u>:^[7]

This reaction, which was discovered around 1898, remains of interest in nitric

oxide <u>prodrug</u> research. Nitric oxide can also react directly with <u>sodium methoxide</u>, forming <u>sodium formate</u> and <u>nitrous</u> oxide. [8]

Coordination complexes

Nitric oxide reacts with <u>transition metals</u> to give complexes called <u>metal nitrosyls</u>. The most common bonding mode of nitric oxide is the terminal linear type (M-NO).^[4] Alternatively, nitric oxide can serve as a one-electron pseudohalide. In such complexes, the M-N-O group is

characterized by an angle between 120° and 140°. The NO group can also bridge between metal centers through the nitrogen atom in a variety of geometries.

Production and preparation

In commercial settings, nitric oxide is produced by the <u>oxidation</u> of <u>ammonia</u> at 750–900 °C (normally at 850 °C) with <u>platinum</u> as <u>catalyst</u>:

$$4 \text{ NH}_3 + 5 \text{ O}_2 \rightarrow 4 \text{ NO} + 6 \text{ H}_2\text{O}$$

The uncatalyzed <u>endothermic</u> reaction of oxygen (O₂) and <u>nitrogen</u> (N₂), which is

Reactions

With di- and triatomic molecules

Upon condensing to a liquid, nitric oxide dimerizes to <u>dinitrogen dioxide</u>, but the association is weak and reversible. The N-

effected at high temperature (>2000 °C) by lightning has not been developed into a practical commercial synthesis (see Birkeland-Eyde process):

$$N_2 + O_2 \rightarrow 2 NO$$

Laboratory methods

In the laboratory, nitric oxide is conveniently generated by reduction of dilute <u>nitric acid</u> with <u>copper</u>:

$$8 \text{ HNO}_3 + 3 \text{ Cu} \rightarrow 3 \text{ Cu}(\text{NO}_3)_2 + 4 \text{ H}_2\text{O} + 2 \text{ NO}$$

An alternative route involves the reduction of nitrous acid in the form of sodium nitrite or potassium nitrite:

2 NaNO₂ + 2 NaI + 2 H₂SO₄
$$\rightarrow$$
 I₂ + 2
Na₂SO₄ + 2 H₂O + 2 NO
2 NaNO₂ + 2 FeSO₄ + 3 H₂SO₄ \rightarrow
Fe₂(SO₄)₃ + 2 NaHSO₄ + 2 H₂O + 2 NO
3 KNO₂ + KNO₃ + Cr₂O₃ \rightarrow 2 K₂CrO₄ + 4
NO

The iron(II) sulfate route is simple and has been used in undergraduate laboratory experiments. So-called <u>NONOate</u>

$$\cdot$$
NO + HO₂' \rightarrow 'NO₂ + 'OH
 \cdot NO₂ + 'OH \rightarrow HNO₃

Nitric acid, along with <u>sulfuric acid</u>, contributes to <u>acid rain</u> deposition.

Ozone depletion

·NO participates in <u>ozone layer depletion</u>. Nitric oxide reacts with stratospheric <u>ozone</u> to form O₂ and nitrogen dioxide:

$$\cdot NO + O_3 \rightarrow NO_2 + O_2$$

This reaction is also utilized to measure concentrations of ·NO in control volumes.

Environmental effects

Acid rain deposition

Nitric oxide reacts with the hydroperoxy radical (HO₂*) to form nitrogen dioxide (NO₂), which then can react with a hydroxyl radical (<u>*OH</u>) to produce <u>nitric acid</u> (HNO₃):

Nitric oxide NO

NO is a colourless gas and is an important intermediate in the manufacture of nitric acid by the catalytic oxidation of ammonia (Ostwald process). It

THE GROUP 15 ELEMENTS

was also important in the obsolete Birkeland-Eyde process which involved sparking dinitrogen and dioxygen. NO is prepared in the laboratory by the reduction of dilute HNO₃ with Cu, or reduction of HNO₂ with I⁻:

$$3Cu + 8HNO_3 \rightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$$

 $2HNO_2 + 2I^- + 2H^+ \rightarrow 2NO + I_2 + 2H_2O$

NO is a neutral oxide and is not an acid anhydride.

NO has 11 valency electrons. It is impossible for them all to be paired, and hence this is an odd electron molecule and the gas is paramagnetic. It is diamagnetic in the liquid and solid states, because the molecule dimerizes, forming O—N—N—O. The asymmetrical dimer O—N—O—N has been observed to be formed as a red solid in the presence of HCl or other Lewis acids.

The bond length N—O is 1.15 Å, which is intermediate between a double and a triple bond. Bonding is best described using the molecular orbital theory (see Chapter 4). The bonding is similar to that in N_2 and CO which both have 10 outer electrons. NO has 11 outer electrons, and the extra unpaired electron occupies an antibonding π^*2p orbital. This reduces the bond order from 3 in N_2 to $2\frac{1}{2}$ in NO. If this electron is removed by oxidizing NO, the nitrosonium ion NO⁺ is formed. In NO⁺ the bond order is 3, and the N—O bond length contracts from 1.15 Å in NO to 1.06 Å in NO⁺.

Odd electron molecules are usually highly reactive and tend to dimerize. NO is unusually stable for an odd electron molecule. Nevertheless it reacts instantly with dioxygen to give NO₂, and with the halogens it gives nitrosyl halides, e.g. NOCl.

$$2NO + O_2 \rightarrow 2NO_2$$

 $2NO + Cl_2 \rightarrow 2NOCl$

NO readily forms coordination complexes with transition metal ions. These complexes are called nitrosyls. Fe²⁺ and NO form the complex [Fe(H₂O)₅NO]²⁺, which is responsible for the colour in the 'brown-ring test' for nitrates. Most nitrosyl complexes are coloured. Another example is sodium nitroprusside Na₂[Fe(CN)₅NO] · 2H₂O. NO often acts as a three-electron donor, in contrast to most ligands which donate two electrons. Thus three CO groups may be replaced by two NO groups:

$$[Fe(CO)_5] + 2NO \rightarrow [Fe(CO)_2(NO)_2] + 3CO$$

$$[Cr(CO)_6] + 4NO \rightarrow [Cr(NO)_4] + 6CO$$
In these complexes the Manning of the Manni

In these complexes the M—N—O atoms are linear, or close to linear. However, in 1968 the M—N—O angle in $[Ir(CO)(Cl)(PPh_3)(NO)]^+$ was found to be 123°, and since then a number of other complexes have been found with bond angles in the range 120–130°. These bent bonds, which are weaker than straight bonds, are of considerable theoretical interest. NO may also act as a bridging ligand between two or three metal atoms in a similar way to CO.