Nitrogen Dioxide

One of the gases in smog.

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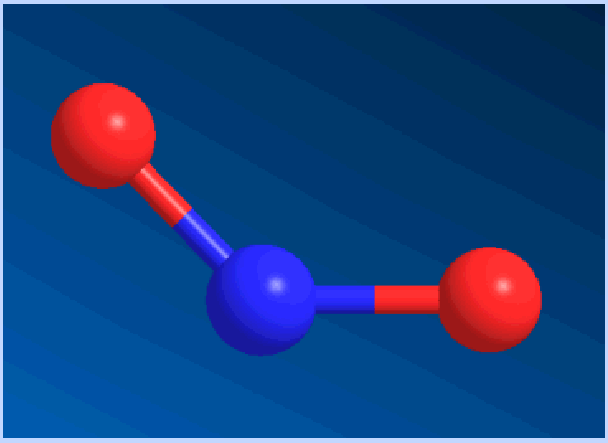
Molecule of the Month December 2012
Also available: JSMol version.



Tell me something about nitrogen dioxide...

Of course, it was John Lennon's favourite molecule.

Go on then, why was it John Lennon's favourite molecule?

Because it is ONO...

ONO!

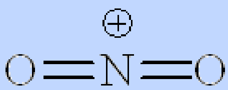
Yes, that is the sequence of atoms in nitrogen dioxide. O-N-O.

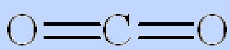
Just like carbon dioxide?

Except that NO_2 is a V-shaped molecule, and CO_2 is linear.

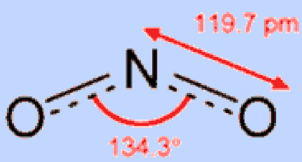
Why are NO_2 and CO_2 different shapes?

At first sight, NO_2 seems similar to CO_2, carbon dioxide. But an NO_2 molecule contains one more electron than CO_2. If an electron is removed from NO_2, you get the NO_2^+ (nitronium or nitryl) ion. It is isoelectronic with CO_2, having two N=O double bonds and no unpaired electrons, so repulsion between the two regions of electron density is minimised by the 180° bond angle, and it is linear, as with CO_2.

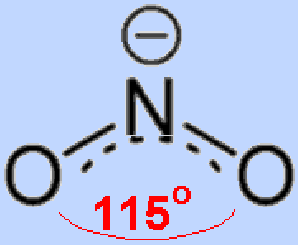




Neutral NO_2 has one more electron, which is accommodated in an orbital on the nitrogen atom. This introduces extra repulsions. The single-electron region is not as electron-rich as the N-O multiple bonds, so it does not have their repulsive power. Thus the bond angle is 134°, rather than the 120° expected if the repulsions between the electron-rich areas were identical.



NO_2^- has one more electron than NO_2, so it has a non-bonding pair ("lone pair") of electrons on nitrogen. This exerts a greater repulsion than the single electron in NO_2, so the O-N-O angle is reduced further, to 115.4°.

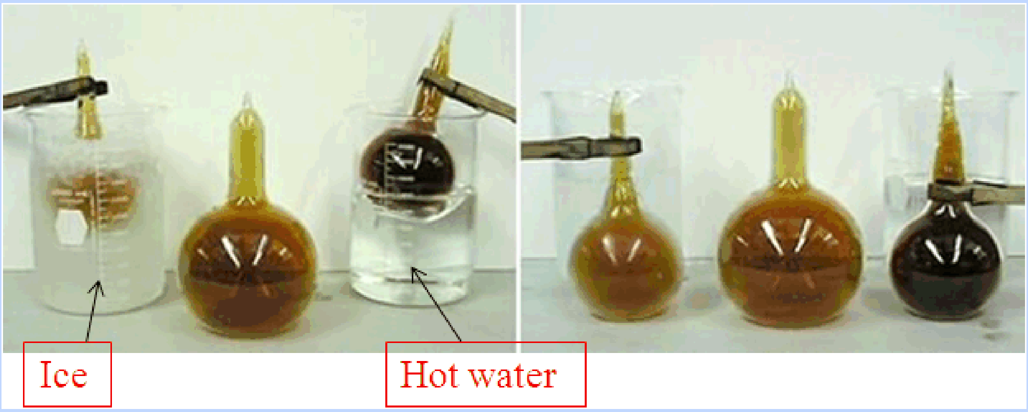


Nitrite ion with an O-N-O bond angle of 115.4° (according to Gillespie and Hargittai).

In what other ways does NO_2 differ from CO_2?

The odd electron extra makes NO_2 a free radical, and so much more reactive than CO_2. One obvious example lies in what happens when NO_2 is cooled.

$$2\ NO_2 \rightarrow N_2O_4$$



The colour change as NO_2 dimerises.

If you cool NO_2 gas down, its colour gets much paler. Eventually it changes from a brown gas to a colourless liquid. Two NO_2 radicals have each donated their unpaired electron to form a rather weak N-N covalent bond, linking them to make a N_2O_4 molecule. Conversely, when the liquid N_2O_4 is warmed up, it boils at 21°C forming a brown gas, containing some NO_2; the more it is warmed, the browner it gets until by 140°C all the N_2O_4 has split into NO_2. The process is quite reversible; the equilibrium can be shifted by changing the pressure on a mixture of those gases, so at high pressure the colour gets paler as NO_2 is converted to N_2O_4.

$$2\ NO_2 \rightleftharpoons N_2O_4$$

Are there any other differences between NO_2 and CO_2?

Nitrogen is a very unreactive element, but during thunderstorms the temperature close to a lightning strike is several thousand degrees, quite hot enough to make nitrogen and oxygen molecules react to form NO.

$$N_2 + O_2 \rightarrow 2\ NO$$

As the air cools, the NO reacts with more oxygen to turn into NO_2. This reaction is reversed on heating.

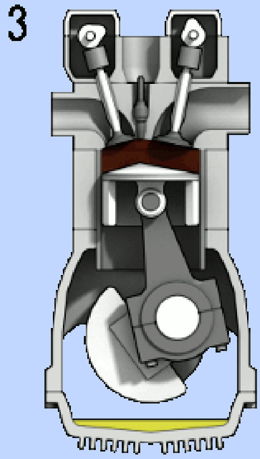
$$2\ NO + O_2 \rightarrow 2\ NO_2$$

The first reaction also occurs in internal combustion engines, where the temperature reaches around 2000°C, then leading to release of cooled gases containing NO_2 into the exhaust system and potentially into the atmosphere (see image, right).

One of the jobs of an automobile catalytic converter is to break down nitrogen oxides (whether NO or NO_2) into non-toxic gases, nitrogen and oxygen.

$$2NO_x \rightarrow xO_2 + N_2$$

Nitrogen oxides are often referred to collectively as NO_x.



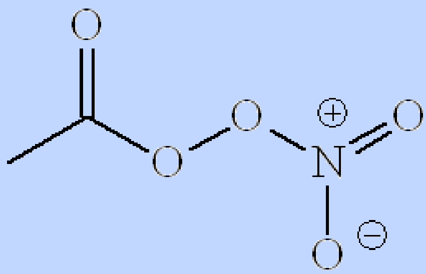
Brown smog over Sao Paulo, Brazil.

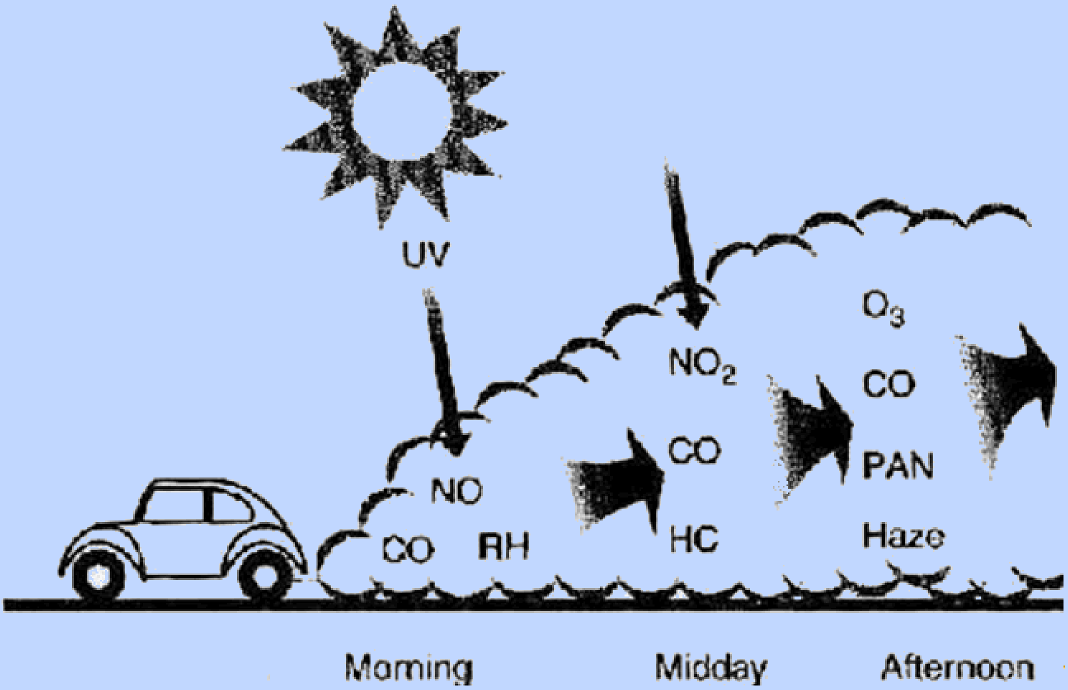
In the days before catalytic converters, any NO_x from car engines went straight into the atmosphere. From a distance, the air in some big "polluted" cities today can still have a brown tint. Obviously, this is bad, because of the toxicity of the NO_2, but it also causes other pollutants. In the presence of oxygen, sunlight turns unburnt hydrocarbons from car exhausts into molecules like aldehydes and ketones; on further reaction, they form peroxyacyl radicals, which react with NO_2 forming peroxyacyl nitrates (PANs).

Nothing to do with the Greek God?

No, on the right is acetylperoxyacylnitrate, the most common PAN.

These are the molecules which can make your eyes water on a busy urban street on a hot, sunny, summer's day. Plant emissions of isoprene get turned into methylvinyl ketone and thence into PANs. PANs are said to damage vegetation and to cause skin cancer. They are also involved in the formation of ozone up in the troposphere.





Does NO_2 have any uses at all, or is it just nasty?

Liquified NO_2, which of course is the dimer N_2O_4, was the fuel oxidant, one component that powered the United States' Titan rockets, used to send the 1960s Project Gemini manned flights into space. Subsequently the Titans launched the unmanned probes to Mars, Jupiter, Saturn, Uranus and Neptune. When the N_2O_4 was mixed with the other component, a combination of hydrazine and 1,1-dimethylhydrazine, the fuel spontaneously ignited forming a lot of very hot steam, CO_2 and N_2. Blast off! Usually things went well, but an error in the final stage of the Apollo-Soyuz test project in 1975 meant that NO_2 entered the spacecraft, and this nearly killed the crew. The photo to the right shows a launch of a Titan rocket, with lots of brown NO_2 being exhausted.

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Back to Molecule of the Month page. [DOI:10.6084/m9.figshare.5255788]