Chem Factsheet

www.curriculum-press.co.uk Number 254

The Oxides of Nitrogen

To succeed in this topic you need to:
- Be familiar with dot and cross diagrams (Lewis structures).
- Be familiar with electronic configurations.
- Be familiar with how to work out oxidation states.

After working through this Factsheet you will:
- Be aware of the variety of oxides formed by nitrogen.
- Know the main natural and man-made sources of these oxides.
- Be aware of the environmental impacts of these oxides.
- Know about possible control measures.

Introduction

Nitrogen forms a total of eight molecular oxides, in which nitrogen exhibits oxidation states ranging from +1 to +5. Of these, the most stable (and, therefore, most familiar) are N_2O (nitrous oxide), NO (nitric oxide), and NO_2 (nitrogen dioxide). The others are N_2O_3, N_2O_5, NO_3, and the dimers of NO and NO_2.

NO and NO_2 are both radicals, each possesses an unpaired electron, and have a tendency to dimerise, forming $(NO)_2$ and N_2O_4 respectively.

$2NO \rightleftharpoons (NO)_2$ $\quad\quad$ $2NO_2 \rightleftharpoons N_2O_4$

At room temperature and pressure, these equilibria lie far to the left which suggests that both radicals are unusually stable.

How does the fact that NO and NO_2 are radicals explain their tendency to dimerise?

Radicals are species (molecules or ions) with an unpaired electron. Such species can dimerise by the sharing of the unpaired electron between two molecules.

Nitrous Oxide, N_2O

The bonding in nitrous oxide, also called nitrogen(I) oxide, is best represented as a resonance hybrid.

> Resonance is a way of describing delocalised electrons within molecules where the bonding cannot be expressed by one single Lewis structure. A molecule with such delocalised electrons is represented by several contributing structures. The actual molecular structure is an approximate intermediate between the contributing forms, called the resonance hybrid.

:N≡N⁺-O:⁻ ↔ :N⁻=N⁺=O

This gas is used as an anaesthetic for minor operations, especially in dentistry, and also as a propellant in cans of whipped cream. This latter use stems from the high solubility of N_2O in fat; the N_2O is mixed in liquid form with the liquid cream inside the canister, displacing any oxygen, which stops the cream from going rancid. Its use as an anaesthetic has given rise to it being known as laughing gas, as its intoxicating effects can include uncontrollable giggling!

Nitrous oxide is naturally present in tiny quantities in our atmosphere as a result of various processes involved in the nitrogen cycle. Although its atmospheric abundance is only about a thousandth of CO_2's, it has a global warming potential almost 300 times greater. It is also very long-lasting with a lifetime in the atmosphere of over 100 years.

Although the amount in the atmosphere is still tiny, it has increased by nearly 20% since the industrial revolution, with one source being the burning of fossil fuels. However the major contributor to atmospheric N_2O is thought to be the widespread use of nitrogenous fertilisers.

Nitric Oxide, NO

The bonding in nitric oxide (nitrogen(II) oxide) can also be represented by a resonance hybrid of two contributing structures.

:N=O: ↔ :N⁻=O⁺

In the liquid and solid states, it has been shown to exist as dimers of $(NO)_2$.

NO can be prepared in the laboratory by reacting copper with concentrated (50%) nitric acid.

$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu^{2+}(aq) + 6NO_3^-(aq) + 4H_2O(l) + 2NO(g)$

Useful revision of half-equations and redox is possible here by identifying the changes in oxidation state that are taking place and by writing separate half equations for the reduction and oxidation processes.

$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu^{2+}(aq) + 6NO_3^-(aq) + 4H_2O(l) + 2NO(g)$

0 $\quad$ 1+5-2 $\quad$ +2 $\quad$ +5 -2 $\quad$ +1 -2 $\quad$ +2-2

Cu is oxidised by the action of the nitrate(V) ion, NO_3^-. The simultaneous reduction of the nitrogen from +5 to +2 yields NO as a product.

NO is produced naturally in the atmosphere by reaction between nitrogen and oxygen in the vicinity of lightning strikes, and also during the combustion of fossil fuels as a result of the high temperature generated in furnaces and internal combustion engines.

$N_2 + O_2 \rightarrow 2NO$

Why is a high temperature needed to bring about reaction between nitrogen and oxygen in the atmosphere?

The activation energy, E_a, for the reaction is high due to the strength of the N≡N bond (+944 kJ mol^{-1})

In the atmosphere, NO is oxidised to NO_2, which then undergoes disproportionation in water to form nitrous and nitric acids, HNO_2 and HNO_3 respectively, that contribute to acid rain. It also contributes to the formation of acid rain through its catalytic role in the oxidation of SO_2.

$NO + ½O_2 \rightarrow NO_2$

$NO_2 + SO_2 \rightarrow NO + SO_3$

$SO_3 + H_2O + ½O_2 \rightarrow H_2SO_4$

NO also contributes to ozone depletion.

$NO + O_3 \rightarrow NO_2 + O_2$

This is followed by a combination of the following processes:

NO_2 (+ UV) $\rightarrow$ NO + O

$NO_2 + O \rightarrow NO + O_2$

$NO_2 + O_3 \rightarrow NO + 2O_2$

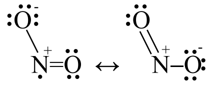
In each case, the regeneration of NO indicates that its role is catalytic.

These negative environmental effects are the reason that NO is removed from exhaust gases in cars by using catalytic converters.

$CO + NO \rightarrow CO_2 + ½N_2$

Nitrogen Dioxide, NO_2

The bonding in nitrogen(IV) oxide, NO_2, is also a resonance hybrid of two contributing structures.



At low temperatures, NO_2 is almost completely dimerised as colourless N_2O_4 but the extent of dissociation of the dimer increases with increasing temperature. The colour darkens as reddish-brown NO_2 is formed.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +ve$
colourless red-brown

This reaction can be used as a good laboratory demonstration of Le Chatelier's principle. If a sample of NO_2 is generated by heating a metal nitrate it can be collected in a gas syringe, which is then sealed.

The effect of pressure can be demonstrated by depressing the plunger and observing the colour changes, then pulling the plunger out and again observing the colour.

With the gas syringe immersed in a water bath, the effect of temperature can also be demonstrated. This can be extended to a quantitative exercise by taking a series of readings of volume and temperature and then plotting a graph of PV against T and comparing with the horizontal line predicted by the ideal gas equation.

NO_2 is very soluble in water, reacting to form a mixture of nitrous and nitric acids (also known as nitric(III) and nitric(V) acids respectively).

$2NO_2(aq) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$

Like NO, NO_2 is produced during fossil fuel combustion and is also produced by various natural processes including bacterial respiration, volcanoes and lightning.

In addition to the contribution it makes to acid rain, NO_2 can also cause respiratory problems and in areas of high concentration, such as near busy roads, prolonged exposure can be a problem for asthmatics.

NO_2 can also contribute to the formation of photochemical smog and ground-level ozone.

NO_2 is also removed from car exhaust fumes in the catalytic converter so as to reduce its environmental impact.

$NO_2 + 2CO \rightarrow 2CO_2 + ½N_2$

Noxer Blocks

Noxer blocks are specialised paving blocks with a coating of titanium dioxide, TiO_2. The TiO_2 surface acts a catalyst for the oxidation of NO and NO_2 in the presence of sunlight and water. The TiO_2 catalyst aids in the production of hydroxyl (OH•), and superoxide ($O_2^{-\bullet}$) radicals that react with NO and NO_2 oxidising them to harmless nitrate(V) ions, NO_3.

Dinitrogen Trioxide, N_2O_3

This unstable oxide exists as a pale blue solid at low temperatures and can be formed by condensing an equimolar mixture of NO and NO_2 at –20 °C. The liquid formed is pale blue and contains an equilibrium mixture of N_2O_3 with NO and NO_2. Dissociation of N_2O_3 into NO and NO_2 is about 90% complete at room temperature.

Dinitrogen Pentoxide, N_2O_5

This colourless solid can be made by dehydrating nitric acid with phosphorous(V) oxide. The solid is actually ionic, $NO_2^+NO_3^-$ (nitronium nitrate) but it adopts a molecular structure in the gaseous state.

Nitrogen Trioxide, NO_3

This highly unstable radical can be formed by thermal or photolytic decomposition of N_2O_5 and is thought to be a trigonal planar molecule.

Questions

1. Draw a dot-and-cross diagram to represent the bonding in a molecule of N_2O. Show outer electrons only.
2. Use your answer in (1) to state and explain the shape and bond angle of a molecule of N_2O.
3. Explain why nitrogen is so unreactive.
4. Explain why the conditions in a car engine lead to the production of oxides of nitrogen.
5. By using oxidation states, explain why the formation of nitrous and nitric acids from nitrogen dioxide, NO_2, is described as a disproportionation reaction.

Answers

1. One of

A N=N=O

B :N≡N–O:

C :N–N≡O:

2. Linear shape / 180° bond angle.
   Two regions/groups of electrons/electron density/negative-charge centres/electron domains around central N.
3. Strong triple bond in N_2 molecule requires a lot of energy to break. Activation energy of reactions involving nitrogen molecules is very high.
4. High temperature provides the energy required for N_2 molecules to overcome the activation energy barrier and break the triple bond.
5. Oxidation state of N in NO_2 is +4, in HNO_2 is +3 and in HNO_3 is +5. The nitrogen atoms undergo simultaneous oxidation (+4 to +5) and reduction (+4 to +3).

Acknowledgements: *This Factsheet was researched and written by* ***Tony Tooth*** *and published in* ***September 2016*** *by* ***Curriculum Press****, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU.* ***Chem Factsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber.* ***ISSN 1351-5136***