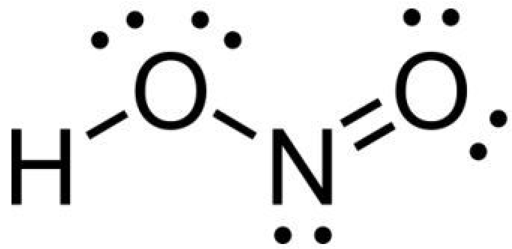
# *Nitrous acid*

**Nitrous acid** (molecular formula $HNO_2$) is a weak and monobasic acid known only in solution, in the gas phase and in the form of nitrite ($NO_2^-$) salts.[1] Nitrous acid is used to make diazonium salts from amines. The resulting diazonium salts are reagents in azo coupling reactions to give azo dyes.

**Nitrous acid**




**Names**

Preferred IUPAC name

Nitrous acid

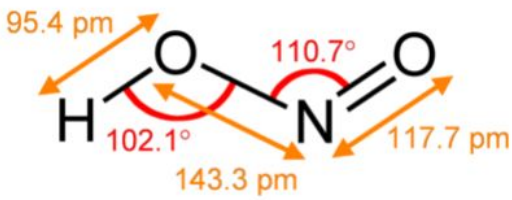
Systematic IUPAC name

Hydroxidooxidonitrogen

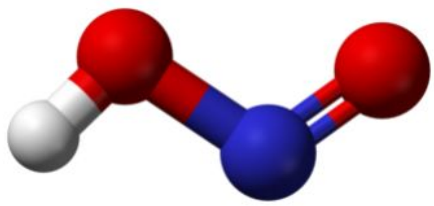
| | |
|---|---|
| Appearance | Pale blue solution |
| Density | Approx. 1 g/ml |
| Melting point | Only known in solution or as gas |
| Acidity ($pK_a$) | 3.398 |
| Conjugate base | Nitrite |
| **Hazards** | |
| **NFPA 704** (fire diamond) |  |
| Flash point | Non-flammable |

## Structure

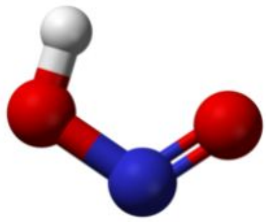
In the gas phase, the planar nitrous acid molecule can adopt both a *cis* and a *trans* form. The *trans* form predominates at room temperature, and IR measurements indicate it is more stable by around 2.3 kJ/mol.[1]




Dimensions of the *trans* form
(from the microwave spectrum)



Model of the *trans* form



*cis* form

# Preparation

Nitrous acid is usually generated by acidification of aqueous solutions of sodium nitrite with a mineral acid. The acidification is usually conducted at ice temperatures, and the $HNO_2$ is consumed in situ.[2][3] Free nitrous acid is unstable and decomposes rapidly.

Nitrous acid can also be produced by dissolving dinitrogen trioxide in water according to the equation

$$N_2O_3 + H_2O \rightarrow 2\ HNO_2$$

# Reactions

## Decomposition

Gaseous nitrous acid, which is rarely encountered, decomposes into nitrogen dioxide, nitric oxide, and water:

$$2\ HNO_2 \rightarrow NO_2 + NO + H_2O$$

Nitrogen dioxide disproportionates into nitric acid and nitrous acid in aqueous solution:[4]

$$2\ NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

In warm or concentrated solutions, the overall reaction amounts to production of nitric acid, water, and nitric oxide:

$$3\ HNO_2 \rightarrow HNO_3 + 2\ NO + H_2O$$

The nitric trioxide can subsequently be re-oxidized by air to nitric acid, making the overall reaction:

$$2\,HNO_2 + O_2 \rightarrow 2\,HNO_3$$

## Reduction

...

With $I^-$ and $Fe^{2+}$ ions, NO is formed:[5]

$$2\,KNO_2 + 2\,KI + 2\,H_2SO_4 \rightarrow I_2 + 2\,NO + 2\,H_2O + 2\,K_2SO_4$$

$$2\,KNO_2 + 2\,FeSO_4 + 2\,H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2\,NO + 2\,H_2O + K_2SO_4$$

With $Sn^{2+}$ ions, $N_2O$ is formed:

$$2\,KNO_2 + 6\,HCl + 2\,SnCl_2 \rightarrow 2\,SnCl_4 + N_2O + 3\,H_2O + 2\,KCl$$

With $SO_2$ gas, $NH_2OH$ is formed:

$$2\,KNO_2 + 6\,H_2O + 4\,SO_2 \rightarrow 3\,H_2SO_4 + K_2SO_4 + 2\,NH_2OH$$

With Zn in alkali solution, $NH_3$ is formed:

$$5\,H_2O + KNO_2 + 3\,Zn \rightarrow NH_3 + KOH + 3\,Zn(OH)_2$$

With $N_2H_5^+$, $HN_3$, and subsequently, $N_2$ gas is formed:

$$HNO_2 + [N_2H_5]^+ \rightarrow HN_3 + H_2O + H_3O^+$$

$$HNO_2 + HN_3 \rightarrow N_2O + N_2 + H_2O$$

Oxidation by nitrous acid has a kinetic control over thermodynamic control, this is best illustrated that dilute nitrous acid is able to oxidize $I^-$ to $I_2$, but dilute nitric acid cannot.

$$I_2 + 2\,e^- \rightleftharpoons 2\,I^- \qquad E^o = +0.54\ V$$

$$NO_3^- + 3\,H^+ + 2\,e^- \rightleftharpoons HNO_2 + H_2O \qquad E^o = +0.93\ V$$

$$HNO_2 + H^+ + e^- \rightleftharpoons NO + H_2O \qquad E^o = +0.98\ V$$

It can be seen that the values of $E^o_{cell}$ for these reactions are similar, but nitric acid is a more powerful oxidizing agent. Base on the fact that dilute nitrous acid can oxidize iodide into iodine, it can be deduced that nitrous is a faster, rather than a more powerful, oxidizing agent than dilute nitric acid.[5]

## Organic chemistry

Nitrous acid is used to prepare diazonium salts:

$$HNO_2 + ArNH_2 + H^+ \rightarrow ArN_2^+ + 2\,H_2O$$

where Ar is an aryl group.

Such salts are widely used in organic synthesis, e.g., for the Sandmeyer reaction and in the preparation azo dyes, brightly colored compounds that are the basis of a qualitative test for anilines.[6] Nitrous acid is used to destroy toxic and potentially explosive sodium azide. For most purposes, nitrous acid is usually formed *in situ* by the action of mineral acid on sodium nitrite:[7] It is mainly blue in colour

$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$

$$2\,NaN_3 + 2\,HNO_2 \rightarrow 3\,N_2 + 2\,NO + 2\,NaOH$$

Reaction with two α-hydrogen atoms in ketones creates oximes, which may be further oxidized to a carboxylic acid, or reduced to form amines. This process is used in the commercial production of adipic acid.

Nitrous acid reacts rapidly with aliphatic alcohols to produce alkyl nitrites, which are potent vasodilators:

$$(CH_3)_2CHCH_2CH_2OH + HNO_2 \rightarrow (CH_3)_2CHCH_2CH_2ONO + H_2O$$

The carcinogens called nitrosamines are produced, usually not intentionally, by the reaction of nitrous acid with secondary amines:

$$HNO_2 + R_2NH \rightarrow R_2N\text{-}NO + H_2O$$

## Nitrous acid $HNO_2$

Nitrous acid is unstable except in dilute solution. It is easily made by acidifying a solution of a nitrite. Barium nitrite is often used with $H_2SO_4$, since the insoluble $BaSO_4$ can be filtered off easily.

$$Ba(NO_2)_2 + H_2SO_4 \rightarrow 2HNO_2 + BaSO_4$$

Group 1 metal nitrites can be made by heating nitrates, either on their own or with Pb.

$$2NaNO_3 \xrightarrow{\text{heat}} 2NaNO_2 + O_2$$

$$NaNO_3 + Pb \xrightarrow{\text{heat}} NaNO_2 + PbO$$

Nitrous acid and nitrites are weak oxidizing agents and will oxidize $Fe^{2+}$ to $Fe^{3+}$, and $I^-$ to $I_2$: they themselves are reduced to $N_2O$ or NO. However, $HNO_2$ and nitrites are oxidized by $KMnO_4$ and $Cl_2$, forming nitrates $NO_3^-$.

Large amounts of nitrites are used to make diazo compounds, which are converted into azo dyes, and also pharmaceutical products.

$$PhNH_2 + HNO_2 \rightarrow \underset{\text{phenyldiazonium chloride}}{PhN_2Cl} + 2H_2O$$

Nitrites are important in the manufacture of hydroxylamine:

$$NH_4NO_2 + NH_4HSO_3 + SO_2 + 2H_2O \rightarrow [NH_3OH]^+HSO_4^- + (NH_4)_2SO_4$$

Sodium nitrite is used as a food additive in cured meat, sausages, hot dogs, bacon and tinned ham. Though an approved additive, its use is controversial. $NaNO_2$ is slightly poisonous. The tolerance limit for humans is 5–10 g per day depending on body weight. $NO_2^-$ ions inhibit the growth of bacteria, particularly *Clostridium botulinum*, which causes botulism (a particularly unpleasant form of food poisoning). Reductive decomposition of $NO_2^-$ gives NO, which forms a red complex with haemoglobin, and improves the look of meat. There is concern that during the cooking of meat, the nitrites may react with amines and be converted into nitrosamines $R_2N{-}N{=}O$, which are thought to cause cancer. Certainly secondary and tertiary aliphatic amines form nitrosamines with nitrites:

$$Et_2NH + HNO_2 \rightarrow Et_2NNO + H_2O$$

$$Et_3N + HNO_2 \rightarrow [Et_3NH][NO_2] \xrightarrow{heat} Et_2NNO + EtOH$$

The nitrite ion is a good ligand and forms many coordination complexes. Since lone pairs of electrons are present on both N and O atoms, either N or O can form a coordinate bond. This gives rise to isomerism between nitro complexes $M \leftarrow NO_2$ and nitrito complexes $M \leftarrow ONO$, for example $[Co(NH_5)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$. This is discussed in Chapter 7, under 'Isomerism'. If a solution of $Co^{2+}$ ions is treated with $NO_2^-$ ions, first $Co^{2+}$ ions are oxidized to $Co^{3+}$, then $NO_2^-$ ions form the complex $[Co(NO_2)_6]^{3-}$. Precipitation of potassium cobaltinitrite $K_3[Co(NO_2)_6]$ is used to detect $K^+$ qualitatively. The $NO_2^-$ ion may act as a chelating ligand, and bond to the same metal twice, or it may act as a bridging ligand joining two metal atoms.

The nitrite ion $NO_2^-$ has a plane triangular structure, with N at the centre, two corners occupied by O atoms, and the third corner occupied by the lone pair. A three-centre bond covers the N and the two O atoms and the bond order is 1.5 for the N—O bonds, which have bond lengths in between those for a single and double bond. (More details are given in Chapter 4, under 'Examples of molecular orbital treatment involving delocalised $\pi$ bonding'.)