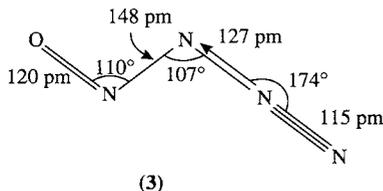


11.3.6 Oxides of nitrogen

Nitrogen is unique among the elements in forming no fewer than 8 molecular oxides, 3 of which are paramagnetic and all of which are thermodynamically unstable with respect to decomposition into N_2 and O_2 . In addition there is evidence for fugitive species such as nitryl azide, N_3NO_2 , but this decomposes rapidly below room temperature⁽⁹⁹⁾ and will not be considered further. Three of the oxides (N_2O , NO and NO_2) have been known for over 200 y and were, in fact, amongst the very first gaseous compounds to be isolated and identified (J. Priestley and others in the 1770s). The most recent addition, nitrosyl azide N_4O (p. 433), was isolated in 1993 as a pale yellow solid whose vibration spectrum at -110° is consistent with the optimized computed structure (3).⁽⁸⁴⁾



The physiological effects of N_2O (laughing gas, anaesthetic) and NO_2 (acid, corrosive fumes) have been known from the earliest days, and the environmental problems of “ NO_x ” from automobile exhaust fumes and as a component in photochemical smog are well known in all industrial countries.^(100,101)

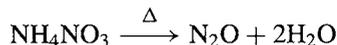
NO is now recognized as a key neuro transmitter in humans and other animals and its biologically triggered synthesis is implicated in cardiovascular pharmacology, hypertension, impotence, immunology and other vital functions.⁽¹⁰²⁾ NO and NO_2 are important in

the commercial production of nitric acid (p. 466) and nitrate fertilizers and N_2O_4 has been used extensively as the oxidizer in rocket fuels for space missions (p. 429).

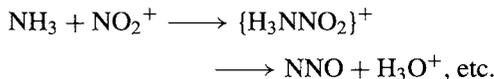
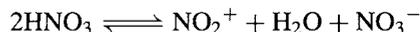
The oxides of nitrogen played an important role in exemplifying Dalton’s law of multiple proportions which led up to the formulation of his atomic theory (1803–8), and they still pose some fascinating problems in bonding theory. Their formulae, molecular structure, and physical appearance are briefly summarized in Table 11.7 and each compound is discussed in turn in the following sections.

Nitrous oxide (Dinitrogen monoxide), N_2O

Nitrous oxide can be made by the careful thermal decomposition of molten NH_4NO_3 at about $250^\circ C$:



Although the reaction has the overall stoichiometry of a dehydration it is more complex than this and involves a mutual redox reaction between N^{-III} and N^V . This is at once explicable in terms of the volt-equivalent diagram in Fig. 11.9 which also interprets why NO and N_2 are formed simultaneously as byproducts. It is probable that the mechanism involves dissociation of NH_4NO_3 into NH_3 and HNO_3 , followed by autoprotolysis of HNO_3 to give NO_2^+ , which is the key intermediate:



Consistent with this ^{15}NNO can be made from $^{15}NH_4NO_3$, and $N^{15}NO$ from $NH_4^{15}NO_3$. Alternative preparative routes (Fig. 11.9) are the reduction of aqueous nitrous acid with either hydroxylamine or hydrogen azide:

and D. J. STUEHR, *Chem. and Eng. News*, 26–38, 20 December 1993. C. R. TIGGLE, *Pharmaceutical News* 1 (3), 9–14 (1994).

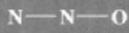
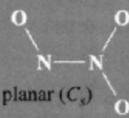
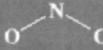
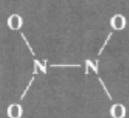
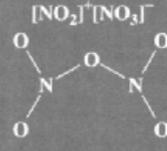
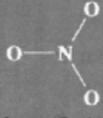
⁹⁹ M. P. DOYLE, J. J. MACIEJKO and S. C. BUSMAN, *J. Am. Chem. Soc.* **95**, 952–3 (1973).

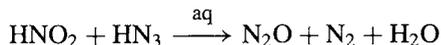
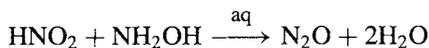
¹⁰⁰ S. D. LEE (ed.), *Nitrogen Oxides and their Effects on Health*, Ann Arbor Publishers, Michigan, 1980, 382 pp.

¹⁰¹ H. BOSCH and F. J. J. JANSSEN, *Catalytic Reduction of Nitrogen Oxides*, Elsevier, Amsterdam, 1988, 164 pp.

¹⁰² K. CULOTTA and D. E. KOSHLAND, *Science* **258**, 1862–5 (1992). J. S. STAMLER, D. J. SINGEL and J. S. LOSCALZO, *Science* **258**, 1898–901 (1992). P. L. FELDMAN, O. W. GRIFFITH

Table 11.7 The oxides of nitrogen (See also structure 3, p. 443)

Formula	Name	Structure	Description
N ₂ O	Dinitrogen monoxide (nitrous oxide)	 linear (C _{∞v})	Colourless gas (bp -88.5°) (cf. isoelectronic CO ₂ , NO ₂ ⁺ , N ₃ ⁻)
NO	(Mono) nitrogen monoxide		Colourless paramagnetic gas (bp -151.8°); liquid and solid are also colourless when pure
N ₂ O ₃	Dinitrogen trioxide	 planar (C _s)	Blue solid (mp -100.7°), dissociates reversibly in gas phase into NO and NO ₂
NO ₂	Nitrogen dioxide	 bent (C _{2v})	Brown paramagnetic gas, dimerizes reversibly to N ₂ O ₄
N ₂ O ₄	Dinitrogen tetroxide	 planar D _{2h}	Colourless liquid (mp -11.2°) dissociates reversibly in gas phase to NO ₂
N ₂ O ₅	Dinitrogen pentoxide	 planar C _{2v} (~D _{2h})	Colourless ionic solid; sublimes at 32.4° to unstable molecular gas (angle N—O—N ~180°)
NO ₃	Nitrogen trioxide	 planar (D _{3h})	Unstable paramagnetic radical



Thermal decomposition of nitramide, H₂NNO₂, or hyponitrous acid H₂N₂O₂ (both of which have the empirical formula N₂O.H₂O) have also been used. The mechanisms of these and other reactions involving simple inorganic compounds of N have been reviewed.⁽¹⁰³⁾

However, though N₂O can be made in this way it is not to be regarded as the anhydride of hyponitrous acid since H₂N₂O₂ is not formed when N₂O is dissolved in H₂O (a similar relation exists between CO and formic acid).

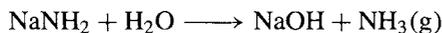
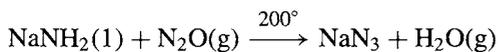
Nitrous oxide is a moderately unreactive gas comprised of linear unsymmetrical molecules, as expected for a 16-electron triatomic species (p. 433). The symmetrical structure N—O—N is precluded on the basis of orbital energetics. Some physical properties are in Table 11.8: it will be seen that the N—N and N—O distances are

¹⁰³ G. STEDMAN, *Adv. Inorg. Chem. Radiochem.* **22**, 114–70 (1979). See also F. T. BONNER and N.-Y. WANG, *Inorg. Chem.* **25**, 1858–62 (1986).

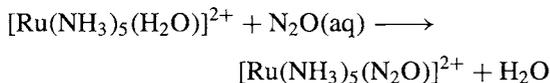
Table 11.8 Some physical properties of N₂O

MP/°C	-90.86	μ/D	0.166
BP/°C	-88.48	Distance (N-N)/pm	112.6
ΔH _f ^o (298 K)/kJ mol ⁻¹	82.0	Distance (N-O)/pm	118.6
ΔG _f ^o (298 K)/kJ mol ⁻¹	104.2		

both short and calculations⁽¹⁰⁴⁾ give the bond orders as N-N 2.73 and N-O 1.61. N₂O is thermodynamically unstable and when heated above ~600°C it dissociates by fission of the weaker bond (N₂O → N₂ + $\frac{1}{2}$ O₂). However, the reaction is much more complex than this simple equation might imply and the process involves a “forbidden” singlet-triplet transition in which electron spin is not conserved.⁽¹⁰⁵⁾ The activation energy for the process is high (~250 kJ mol⁻¹) and at room temperature N₂O is relatively inert: e.g. it does not react with the halogens, the alkali metals or even ozone. At higher temperatures reactivity increases markedly: H₂ gives N₂ and H₂O; many other non-metals (and some metals) react to form oxides, and the gas supports combustion. Perhaps its most remarkable reaction is with molten alkali metal amides to yield azides, the reaction with NaNH₂ being the commercial route to NaN₃ and hence all other azides (p. 433):



It is also notable that N₂O (like N₂ itself) can act as a ligand by displacing H₂O from the aquo complex [Ru(NH₃)₅(H₂O)]²⁺:⁽¹⁰⁶⁾



The formation constant *K* is 7.0 mol⁻¹ l for N₂O and 3.3 × 10⁴ mol⁻¹ l for N₂.

¹⁰⁴ K. JUG, *J. Am. Chem. Soc.* **100**, 6581–6 (1978).

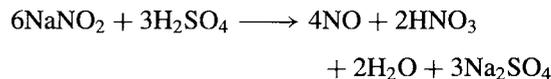
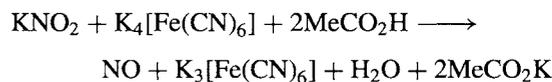
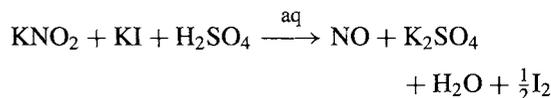
¹⁰⁵ I. R. BEATTIE, Nitrous Oxide, Section 24 in *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 8, pp. 189–215, Supplement 2, Nitrogen (Part 2), Longmans, London, 1967.

¹⁰⁶ J. N. ARMOR and H. TAUBE, *J. Am. Chem. Soc.* **91**, 6874–6 (1969). A. A. DIAMANTIS and G. J. SPARROW, *J. Chem. Soc., Chem. Commun.*, 819–20 (1970). J. N. ARMOR and H. TAUBE, *J. Chem. Soc., Chem. Commun.*, 287–8 (1971).

Notwithstanding the fascinating reaction chemistry of N₂O it is salutary to remember that its largest commercial use is as a propellant and aerating agent for “whipped” ice-cream — this depends on its solubility under pressure in vegetable fats coupled with its non-toxicity in small concentrations and its absence of taste. It was also formerly much used as an anaesthetic.

Nitric oxide (Nitrogen monoxide), NO

Nitric oxide is the simplest thermally stable odd-electron molecule known and, accordingly, its electronic structure and reaction chemistry have been very extensively studied.⁽¹⁰⁷⁾ The compound is an intermediate in the production of nitric acid and is prepared industrially by the catalytic oxidation of ammonia (p. 466). On the laboratory scale it can be synthesized from aqueous solution by the mild reduction of acidified nitrites with iodide or ferrocyanide or by the disproportionation of nitrous acid in the presence of dilute sulfuric acid:



The dry gas has been made by direct reduction of a solid mixture of nitrite and nitrate with chromium(III) oxide (3KNO₂ + KNO₃ + Cr₂O₃ → 4NO + 2K₂CrO₄) but is now more conveniently obtained from a cylinder.

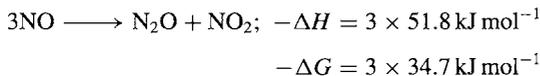
Nitric oxide is a colourless, monomeric, paramagnetic gas with a low mp and bp (Table 11.9). It is thermodynamically unstable and decomposes into its elements at elevated temperatures (1100–1200°C), a fact which militates against its direct synthesis from N₂ and O₂. At high pressures and moderate temperatures

¹⁰⁷ pp. 323–5 of ref. 69.

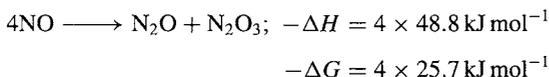
Table 11.9 Some physical properties of NO

MP/°C	-163.6	μ/D	0.15
BP/°C	-151.8	Distance (N-O)/pm	115
ΔH_f° (298 K)/ kJ mol ⁻¹	90.2	Ionization energy/eV	9.23
ΔG_f° (298 K)/ kJ mol ⁻¹	86.6	Ionization energy/ kJ mol ⁻¹	890.6

($\sim 50^\circ$) it rapidly disproportionates:

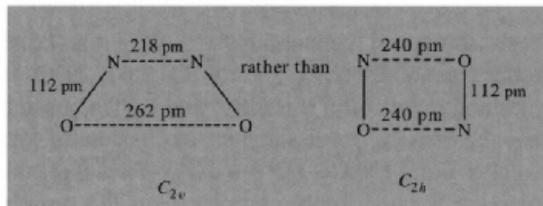


However, when the gas is occluded by zeolites the disproportionation takes a different course:



The molecular orbital description of the bonding in NO is similar to that in N₂ or CO (p. 927) but with an extra electron in one of the π^* antibonding orbitals. This effectively reduces the bond order from 3 to ~ 2.5 and accounts for the fact that the interatomic N–O distance (115 pm) is intermediate between that in the triple-bonded NO⁺ (106 pm) and values typical of double-bonded NO species (~ 120 pm). It also interprets the very low ionization energy of the molecule (9.25 eV, compared with 15.6 eV for N₂, 14.0 eV for CO, and 12.1 eV for O₂). Similarly, the notable reluctance of NO to dimerize can be related both to the geometrical distribution of the unpaired electron over the entire molecule and to the fact that dimerization to O=N–N=O leaves the total bond order unchanged ($2 \times 2.5 = 5$). When NO condenses to a liquid, partial dimerization occurs, the *cis*-form being more stable than the *trans*-. The pure liquid is colourless, not blue as sometimes stated: blue samples owe their colour to traces of the intensely coloured N₂O₃.⁽¹⁰⁸⁾ Crystalline nitric oxide is also colourless (not blue) when pure,⁽¹⁰⁸⁾ and X-ray diffraction data are best interpreted in terms of weak association into

dimeric units. It seems probable that the dimers adopt the *cis*-(C_{2v}) structure⁽¹⁰⁹⁾ rather than the rectangular C_{2h} structure which was at one time favoured,⁽¹¹⁰⁾ i.e.:



In either case each dimer has two possible orientations, and random disorder between these accounts for the residual entropy of the crystal (6.3 J mol⁻¹ of dimer). More recently⁽¹¹¹⁾ an asymmetric dimer $\text{O}=\text{N}-\text{O}=\text{N}$ has been

characterized; this forms as a red species when NO is condensed in the presence of polar molecules such as HCl or SO₂, or Lewis acids such as BX₃, SiF₄, SnCl₄ or TiCl₄. Reaction of NO with either [Pt(PPh₃)₃] or [Pt(PPh₃)₄] yields [Pt(NO)₂(PPh₃)₂] which has been shown by X-ray diffraction analysis to be an unstable planar *cis*-hyponitrite complex, [(PPh₃)₂Pt—ON=NO], with an N=N distance of 121 pm and N–O 132 and 139 pm.⁽¹¹²⁾

The reactivity of NO towards atoms, free radicals, and other paramagnetic species has been much studied, and the chemiluminescent reactions with atomic N and O are important in assaying atomic N (p. 414). NO reacts rapidly with molecular O₂ to give brown NO₂, and this gas is the normal product of reactions which produce NO if these are carried out in air. The oxidation is unusual in following third-order reaction kinetics and, indeed, is the classic

¹⁰⁹ W. N. LIPSCOMB, F. E. WANG, W. R. MAY and E. L. LIPPERT, *Acta Cryst.* **14**, 1100–01 (1961).

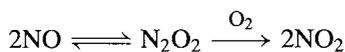
¹¹⁰ W. J. DULMAGE, E. A. MEYERS and W. N. LIPSCOMB, *Acta Cryst.* **6**, 760–4 (1953).

¹¹¹ J. R. OLSEN and J. LAANE, *J. Am. Chem. Soc.* **100**, 6948–55 (1978).

¹¹² S. BHADURI, B. F. G. JOHNSON, A. PICKARD, P. R. RAITHBY, G. M. SHELDRIK and C. I. ZUCCARO, *J. Chem. Soc., Chem. Commun.*, 354–5 (1977).

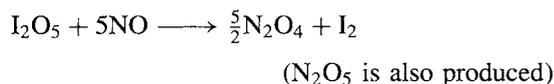
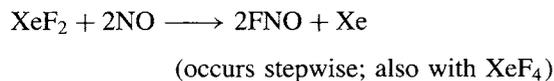
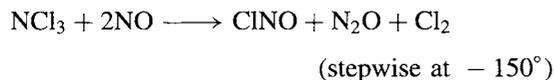
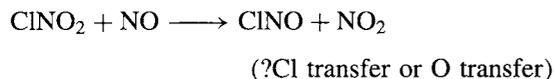
¹⁰⁸ J. MASON, *J. Chem. Educ.* **52**, 445–7 (1975).

example of such a reaction (M. Bodenstein, 1918). The reaction is also unusual in having a negative temperature coefficient, i.e. the rate becomes progressively slower at higher temperatures. For example the rate drops by a factor of 2 between room temperature and 200°. This can be accounted for by postulating that the mechanism involves the initial equilibrium formation of an unstable dimer which then reacts with oxygen:

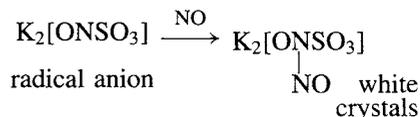
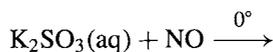
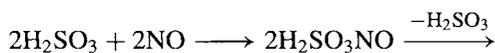


As the equilibrium concentration of N_2O_2 decreases rapidly with increase in temperature the decrease in rate is explained. However alternative mechanisms have also been suggested.⁽¹⁰⁷⁾

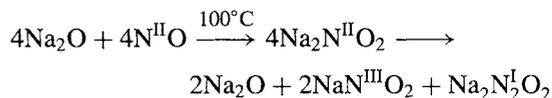
Nitric oxide reacts with the halogens to give XNO (p. 441). Some other facile reactions are listed below:



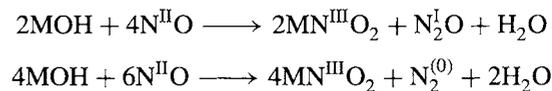
Reactions with sulfides, polysulfides, sulfur oxides and the oxoacids of sulfur are complex and the products depend markedly on reaction conditions (see also p. 745 for blue crystals in chamber acid). Some examples are:



Under alkaline conditions disproportionation reactions predominate. Thus with Na_2O the dioxonitrate(II) first formed, disproportionates into the corresponding nitrite(III) and dioxodinitrate($N-N$)(I) :



With alkali metal hydroxides, both N_2O and N_2 are formed in addition to the nitrite:



Nitric oxide complexes. NO readily reacts with many transition metal compounds to give nitrosyl complexes and these are also frequently formed in reactions involving other oxo-nitrogen species. Classic examples are the "brown-ring" complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ formed during the qualitative test for nitrates, Roussin's red and black salts (p. 1094), and sodium nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$. The field has been extensively reviewed⁽¹¹³⁻¹¹⁵⁾ and only the salient features need be summarized here. A variety of preparative routes is available (see Panel). Most nitrosyl complexes are highly coloured — deep reds, browns, purples, or even black. Apart from the intrinsic interest in the structure and bonding of these compounds there

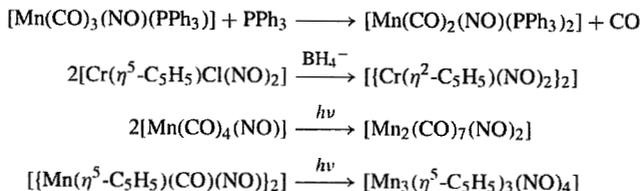
¹¹³ B. F. G. JOHNSON and J. A. McCLEVERTY, *Progr. Inorg. Chem.* **7**, 277-359 (1966). W. P. GRIFFITH, *Adv. Organometallic Chem.* **7**, 211-39 (1968). J. H. ENEMARK and R. D. FELTHAM, *Coord. Chem. Revs.* **13**, 339-406 (1974).

¹¹⁴ K. G. CAULTON, *Coord. Chem. Revs.* **14**, 317-55 (1975). J. A. McCLEVERTY, *Chem. Rev.* **79**, 53-76 (1979).

¹¹⁵ R. EISENBERG and C. D. MEYER, *Acc. Chem. Res.* **8**, 26-34 (1975).

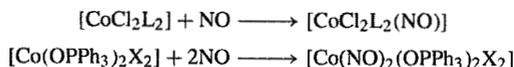
Synthetic Routes to NO Complexes⁽¹¹⁴⁾

The coordination chemistry of NO is often compared to that of CO but, whereas carbonyls are frequently prepared by reactions involving CO at high pressures and temperatures, this route is less viable for nitrosyls because of the thermodynamic instability of NO and its propensity to disproportionate or decompose under such conditions (p. 446). Nitrosyl complexes can sometimes be made by transformations involving pre-existing NO complexes, e.g. by ligand replacement, oxidative addition, reductive elimination or condensation reactions (reductive, thermal or photolytic). Typical examples are:



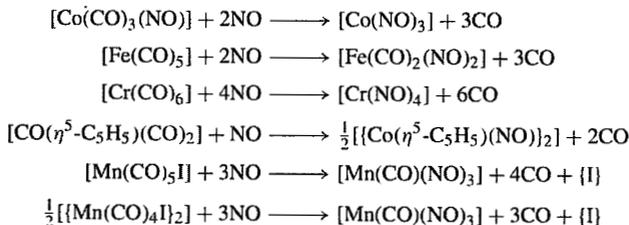
Syntheses which *increase* the number of coordinated NO molecules can be classified into more than a dozen types, of which only the first three use free NO gas.

1. *Addition of NO to coordinatively unsaturated complexes:*

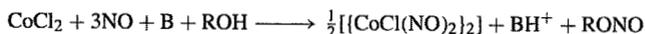


2. *Substitution (ligand replacement)*

Very frequently in these reactions 2NO replace 3CO. Alternatively, 1NO can replace 2CO with simultaneous formation of a metal-metal bond, or 1NO can replace CO + a halogen atom:



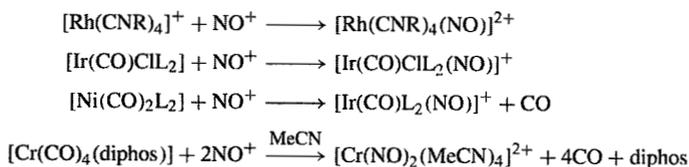
3. *Reductive nitrosylation* (cf. $\text{MF}_6 + \text{NO} \rightarrow \text{NO}^+\text{MF}_6^-$ for Mo, Tc, Re, Ru, Os, Ir, Pt)



where B is a proton acceptor such as an alkoxide or amine.

4. *Addition of or substitution by NO⁺*

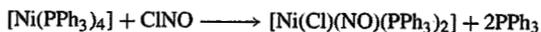
This method uses NOBF₄, NOPF₆, or NO[HSO₄] in MeOH or MeCN, e.g.:



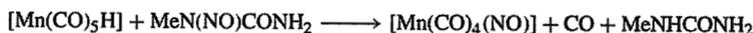
5. *Oxidative addition of XNO*

The reaction may occur with either coordinatively unsaturated or saturated complexes, e.g.:

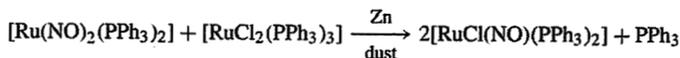




6. Reaction of metal hydride complexes with *N*-nitrosoamides, e.g. *N*-methyl-*N*-nitrosoourea:

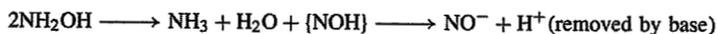


7. Transfer of coordinated *NO* (especially from dimethylglyoximate complexes)

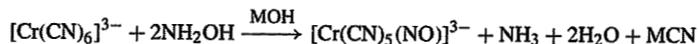


8. Use of NH_2OH in basic solution (especially for cyano complexes)

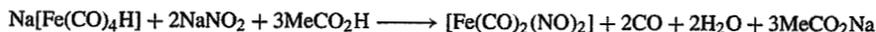
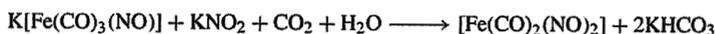
The net transformation can be considered as the replacement of CN^- (or X^-) by NO^- and the reaction can be formally represented as



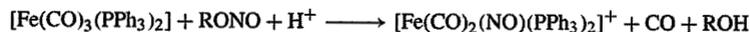
Examples are:



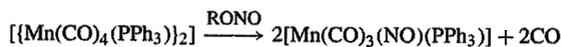
9. Use of acidified nitrites (i.e. $\text{NO}_2^- + 2\text{H}^+ \longrightarrow \text{NO}^+ + \text{H}_2\text{O}$), e.g.:



10. Use of (acidified) nitrites *RONO* (i.e. $\text{RONO} + \text{H}^+ \rightleftharpoons \text{NO}^+ + \text{ROH}$) e.g.:

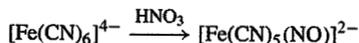
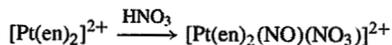


Alternatively in aprotic solvents such as benzene:

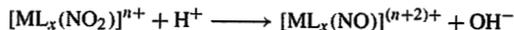


11. Use of concentrated nitric acid (i.e. $2\text{HNO}_3 \rightleftharpoons \text{NO}^+ + \text{NO}_3^- + \text{H}_2\text{O}$)

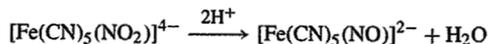
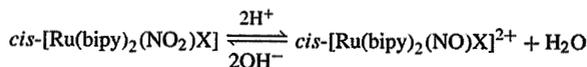
Some of these reactions result, essentially, in the oxidative addition of NO^+NO_3^- to coordinatively unsaturated metal centres whereas in others ligand replacement by NO^+ occurs — this is a favoured route for producing “nitroprusside”, i.e. nitrosylpentacyanoferrate(II):



12. Oxide ion abstraction from coordinated NO_2 , i.e.



e.g.



13. Oxygen atom abstraction



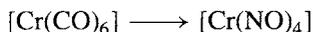
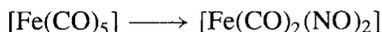
Many variations on these synthetic routes have been devised and the field is still being actively developed. The reactions of NO coordinated to transition metals have been extensively reviewed.⁽¹¹⁴⁾

is much current interest in their potential use as homogeneous catalysts for a variety of chemical reactions.⁽¹¹⁵⁾ See also p. 443.⁽¹⁰²⁾

NO shows a wide variety of coordination geometries (linear, bent, doubly bridging, triply bridging and quadruply bridging — see p. 453) and sometimes adopts more than one mode within the same complex. NO has one more electron than CO and often acts as a 3-electron donor — this is well illustrated by the following isoelectronic series of compounds in which successive replacement of CO by NO is compensated by a matching decrease in atomic number of the metal centre:

[Ni(CO) ₄] mp -25° (colourless)	[Co(CO) ₃ (NO)] -11° (red)	[Fe(CO) ₂ (NO) ₂] +18.4° (deep red)
[Mn(CO)(NO) ₃] +27° (dark green)	[Cr(NO) ₄] decomp > rt (red-black)	

For the same reason 3CO can be replaced by 2NO; e.g.:



In these and analogous compounds the M–N–O group is linear or nearly so, the M–N and N–O distances are short, and the N–O infrared stretching modes usually occur in the range 1650–1900 cm⁻¹. The bonding in such compounds is sometimes discussed in terms of the preliminary transfer of 1 electron from NO to the metal and the coordination of NO⁺ to the reduced metal centre as a “2-electron σ donor, 2-electron π acceptor” analogous to CO (p. 926). This formal scheme, though useful in emphasizing similarities and trends in the coordination behaviour of NO⁺, CO and CN⁻, is unnecessary even for the purpose of “book-keeping” of electrons; it is also misleading in implying an unacceptably large separation of electronic charge in these covalent complexes and in leading to uncomfortably low

oxidation states for many metals. e.g. Cr(–IV) in [Cr(NO)₄], Mn(–III) in [Mn(CO)(NO)₃], etc. Many physical techniques (such as ESCA, Mössbauer spectroscopy, etc.) suggest a much more even distribution of charge and there is accordingly a growing trend to consider linear NO complexes in terms of molecular orbital energy level schemes in which an almost neutral NO contributes 3 electrons to the bonding system via orbitals of σ and π symmetry.⁽¹¹⁶⁾ Nitrogen-15 nmr spectroscopy has also been developed as a powerful tool for characterizing and distinguishing between linear and bent nitrosyl complexes and, where appropriate for studying their interconversion.⁽¹¹⁷⁾

Compounds in which the {M–N–O} group is nominally linear often feature a slightly bent coordination geometry and M–N–O bond angles in the range 165–180° are frequently encountered. However, another group of compounds is known in which the angle M–N–O is close to 120°. The first example, [Co(NO)(S₂CNMe)₂], appeared in 1962⁽¹¹⁸⁾ though there were problems in refining the structure, and a second example was found in 1968⁽¹¹⁹⁾ when the cationic complex [Ir(CO)Cl(NO)(PPh₃)₂]⁺ was found to have a bond angle of 124° (Fig. 11.10); values in the range 120–140° have since been observed in several other compounds (Table 11.10). The related complex [RuCl(NO)₂(PPh₃)₂]⁺, in which the CO ligand has been replaced by a second NO molecule, is interesting in having both

¹¹⁶ H. W. CHEN and W. L. JOLLY, *Inorg. Chem.* **18**, 2548–51 (1979).

¹¹⁷ L. K. BELL, D. M. P. MINGOS, D. G. TEW, L. F. LARKWORTHY, B. SANDELL, D. C. POVEY and J. MASON, *J. Chem. Soc., Chem. Commun.*, 125–6 (1983). L. K. BELL, J. MASON, D. M. P. MINGOS, D. G. TEW, *Inorg. Chem.* **22**, 3497–502 (1983). J. MASON, D. M. P. MINGOS, D. SHERMAN and R. W. M. WARDLE, *J. Chem. Soc., Chem. Commun.*, 1223–5 (1984). J. MASON, D. M. P. MINGOS, J. SCHAEFER, D. SHERMAN and E. O. STEJSKAL, *J. Chem. Soc., Chem. Commun.*, 444–6 (1985). J. BULTITUDE, L. F. LARKWORTHY, J. MASON, D. C. POVEY and B. SANDELL, *Inorg. Chem.* **23**, 3629–33 (1984).

¹¹⁸ P. R. H. ALDERMAN, P. G. OWSTON and J. M. ROWE, *J. Chem. Soc.* 668–73 (1962).

¹¹⁹ D. J. HODGSON and J. A. IBERS, *Inorg. Chem.* **7**, 2345–52 (1968); see also *J. Am. Chem. Soc.* **90**, 4486–8 (1968).

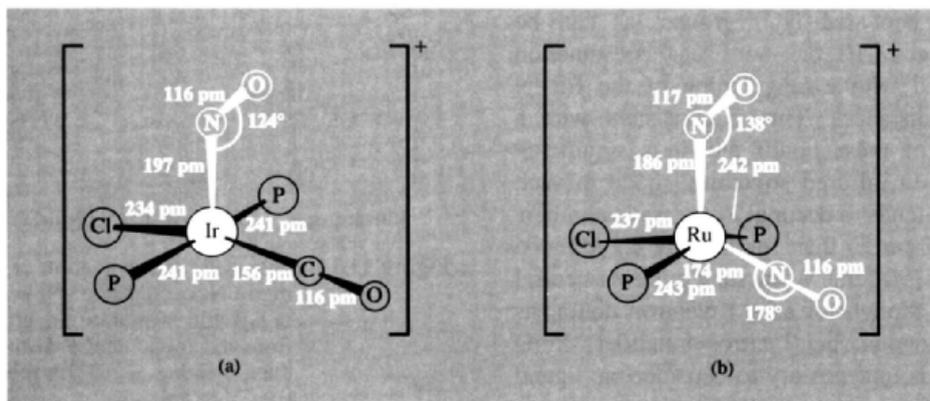


Figure 11.10 Complexes containing bent NO groups: (a) $[\text{Ir}(\text{CO})\text{Cl}(\text{NO})(\text{PPh}_3)_2]^+$, and (b) $[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]^+$. This latter complex also has a linearly coordinated NO group. The diagrams show only the coordination geometry around the metal (the phenyl groups being omitted for clarity).

Table 11.10 Some examples of “linear” and “bent” coordination of nitric oxide

Compound	Angle M–N–O	ν (N–O)/ cm^{-1}
<i>Linear</i>		
$[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$	176°	1630
$[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{NO})_2]$	171°, 166°	1823, 1715
$\text{K}_3[\text{Mn}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$	174°	1700
$[\text{Mn}(\text{CO})_2(\text{NO})(\text{PPh}_3)_2]$	178°	1661
$[\text{Fe}(\text{NO})(\text{mnt})_2]^-$	180°	1867
$[\text{Fe}(\text{NO})(\text{mnt})_2]^{2-}$	165°	1645
$[\text{Fe}(\text{NO})(\text{S}_2\text{CNMe}_2)_2]$	170°	1690
$\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$	178°	1935
$[\text{Co}(\text{diars})(\text{NO})]^{2+}$	179°	1852
$[\text{Co}(\text{Cl})_2(\text{NO})(\text{PMePh}_2)_2]$	165°	1735, 1630
$\text{Na}_2[\text{Ru}(\text{NO})(\text{NO})_2(\text{OH})] \cdot 2\text{H}_2\text{O}$	180°	1893
$[\text{RuH}(\text{NO})(\text{PPh}_3)_3]$	176°	1645
$[\text{Ru}(\text{diphos})_2(\text{NO})]^+$	174°	1673
$[\text{Os}(\text{CO})_2(\text{NO})(\text{PPh}_3)_2]^+$	177°	1750
$[\text{IrH}(\text{NO})(\text{PPh}_3)_3]^+$	175°	1715
<i>Bent</i>		
$[\text{CoCl}(\text{en})_2(\text{NO})]\text{ClO}_4$	124°	1611
$[\text{Co}(\text{NH}_3)_5\text{NO}]^{2+}$	119°	1610
$[\text{Co}(\text{NO})(\text{S}_2\text{CNMe}_2)_2]^{(a)}$	~135°	1626
$[\text{Rh}(\text{Cl})_2(\text{NO})(\text{PPh}_3)_2]$	125°	1620
$[\text{Ir}(\text{Cl})_2(\text{NO})(\text{PPh}_3)_2]$	123°	1560
$[\text{Ir}(\text{CO})\text{Cl}(\text{NO})(\text{PPh}_3)_2]\text{BF}_4$	124°	1680
$[\text{Ir}(\text{CO})\text{I}(\text{NO})(\text{PPh}_3)_2]\text{BF}_4 \cdot \text{C}_6\text{H}_6$	124°	1720
$[\text{Ir}(\text{CH}_3)\text{I}(\text{NO})(\text{PPh}_3)_2]$	120°	1525
<i>Both</i>		
$[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]^+$	178°, 138°	1845, 1687
$[\text{Os}(\text{NO})_2(\text{OH})(\text{PPh}_3)_2]^+$	~180°, 127°	1842, 1632
$[\text{Ir}(\eta^3\text{-C}_3\text{H}_5)(\text{NO})(\text{PPh}_3)_2]^+$ (see text)	~180°, 129°	1763, 1631

mnt = maleonitriedithiolate. diars = 1,2-bis(dimethylarsino)benzene. diphos = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$.

^(a) Value imprecise because of crystal twinning (see ref. 118).

linear and bent $\{M-NO\}$ groups: as can be seen in Fig. 11.10 the nonlinear coordination is associated with a lengthening of the Ru–N and N–O distances. This is consistent with a weakening of these bonds and it is significant that the N–O infrared stretching mode in such compounds tends to occur at lower wave numbers ($1525\text{--}1690\text{ cm}^{-1}$) than for linearly coordinated NO ($1650\text{--}1900\text{ cm}^{-1}$). In such systems neutral NO can be thought of as a 1-electron donor, as in the analogous (bent) nitrosyl halides, XNO (p. 442); it is unnecessary to consider the ligand as an NO^- 2-electron donor. The implication is that the other pair of electrons on NO is placed in an essentially non-bonding orbital on N (which is thus approximately described as an sp^2 hybrid) rather than being donated to the metal as in the linear, 3-electron-donor mode (Fig. 11.11). Consistent with this, non-linear coordination is generally observed with the later transition elements in which the low-lying orbitals on the metal are already filled, whereas linear coordination tends to occur with earlier transition elements which can more readily accommodate the larger number of electrons supplied by the ligand. However, the energetics are frequently finely balanced and other factors must also be considered — a good example is supplied by the two “isoelectronic” complexes shown in Fig. 11.12: $[Co(diars)_2(NO)]^{2+}$ has a linear NO equatorially coordinated to a trigonal bipyramidal cobalt atoms whereas $[IrCl_2(NO)(PPh_3)_2]$ has a bent NO axially coordinated to a square-pyramidal iridium atom, even though both Co and Ir are in the same group in the periodic table. Indeed, the complex cation $[Ir(\eta^3-C_3H_5)(NO)(PPh_3)_2]^+$ shows a facile equilibrium (in CH_2Cl_2 or MeCN solutions) between the linear and the bent NO modes of coordination and, with appropriate counter anions, either the linear --NO (light brown) or bent --NO (red-brown) isomer can be crystallized.⁽¹²⁰⁾ Some further examples of the two coordination geometries are in Table 11.10.

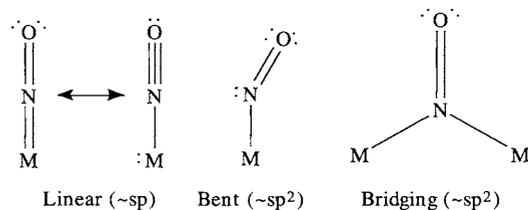


Figure 11.11 Schematic representation of the bonding in NO complexes. Note that bending would withdraw an electron-pair from the metal centre to the N atom thus creating a vacant coordination site: this may be a significant factor in the catalytic activity of such complexes.^(115,121)

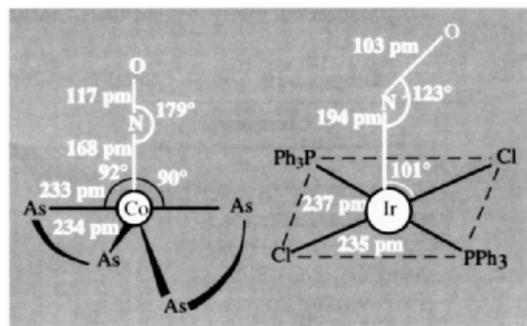


Figure 11.12 Comparison of the coordination geometries of $[Co(diars)_2(NO)]^{2+}$ and $[IrCl_2(NO)(PPh_3)_2]$; diars = 1,2-bis(dimethylarsino)benzene.

Like CO, nitric oxide can also act as a bridging ligand between 2 or 3 metals. Examples are the Cr and Mn complexes in Fig. 11.13. In $[\{Cr(\eta^5-C_5H_5)(NO)(\mu_2-NO)\}_2]$ the linear terminal NO has an infrared band at 1672 cm^{-1} whereas for the doubly bridging NO the vibration drops to 1505 cm^{-1} . In both geometries NO can be considered as a 3-electron donor and there is also a Cr–Cr bond thereby completing an 18-electron configuration around each Cr atom. In $[Mn_3(\eta^5-C_5H_5)_3(\mu_2-NO)_3(\mu_3-NO)]$ the 3 Mn

¹²¹ J. P. COLLMAN, N. W. HOFFMAN and D. E. MORRIS, *J. Am. Chem. Soc.* **91**, 5659–60 (1969). See also F. BOTTOMLEY in P. S. BRATERMAN, *Reactions of Coordinated Ligands*, Vol 2, Plenum Press, New York, 1989, pp. 115–222.

¹²⁰ M. W. SCHOONOVER, E. C. BAKER and R. EISENBERG, *J. Am. Chem. Soc.* **101**, 1880–2 (1979).

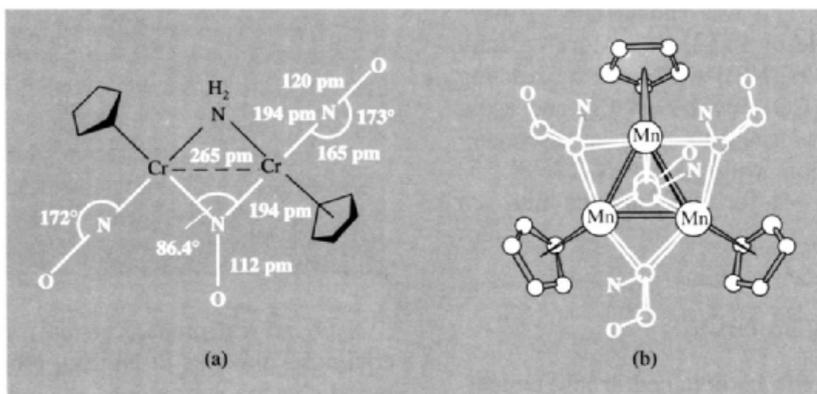


Figure 11.13 Structures of polynuclear nitrosyl complexes: (a) $[\{\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\}_2(\mu_2\text{-NH}_2)(\mu_2\text{-NO})]$ showing linear-terminal and doubly bridging NO; and (b) $[\text{Mn}_3(\eta^5\text{-C}_5\text{H}_5)_3(\mu_2\text{-NO})_3(\mu_3\text{-NO})]$ showing double- and triply-bridging NO; the molecule has virtual C_{3v} symmetry and the average Mn-Mn distance is 250 pm (range 247–257 pm).

form an equilateral triangle each edge of which is bridged by an NO group (ν 1543, 1481 cm^{-1}); the fourth NO is normal to the Mn_3 plane and bridges all 3 Mn to form a triangular pyramid; the N-O stretching vibration moves to even lower wave numbers (1328 cm^{-1}). Again, each metal is associated with 18 valency electrons if each forms Mn-Mn bonds with its 2 neighbours and each NO is a 3-electron donor.

An unprecedented quadruply bridging mode for NO has been established in the violet cluster anion $[\{\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}\}_2(\mu_4\text{-}\eta^2\text{-NO})]^-$ (see Fig. 11.14a).⁽¹²²⁾ The complex was isolated as its $[\text{NEt}_4]^+$ salt after its formation by reaction of NOBF_4 with the trinuclear hydrido anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$. The rather long N-O distance (132–135 pm) is consistent with its formulation as NO^- . Another novel complex is $[\text{Os}(\text{CO})\text{Cl}_2(\text{HNO})(\text{PPh}_3)_2]$ (Fig. 11.14b) which is formed by direct reaction of HCl with $[\text{Os}(\text{CO})(\text{NO})(\text{PPh}_3)_2]$.⁽¹²³⁾ The complex is the first to contain the HNO ligand which is itself thermally unstable as a free molecule. The ligand is N-coordinated and coplanar with the

$[\text{Os}(\text{CO})\text{Cl}_2]$ moiety and has H-N 94 pm, N-O 119 pm and angle HNO 99°.

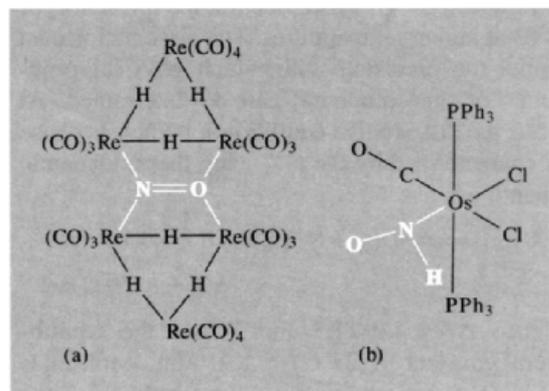


Figure 11.14 (a) Quadruply bridging NO in the anion $[\{\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}\}_2(\mu_4\text{-}\eta^2\text{-NO})]^-$. (b) The neutral complex $[\text{Os}(\text{CO})\text{Cl}_2(\text{HNO})(\text{PPh}_3)_2]$.

In contrast to the numerous complexes of NO which have been prepared and characterized, complexes of the thionitrosyl ligand (NS) are virtually unknown, as is the free ligand itself. The first such complex $[\text{Mo}(\text{NS})(\text{S}_2\text{CNMe}_2)_3]$ was obtained as orange-red air-stable crystals by treating $[\text{MoN}(\text{S}_2\text{CNMe}_2)_3]$ with sulfur in

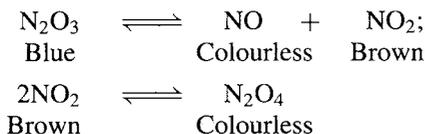
¹²² T. BERINGHELLI, G. CIANI, G. D'ALFONSO, H. MOLINARI, A. SIRONI and M. FRENI, *J. Chem. Soc., Chem. Commun.*, 1327–9 (1984).

¹²³ R. D. WILSON and J. A. IBERS, *Inorg. Chem.* **18**, 336–43 (1979).

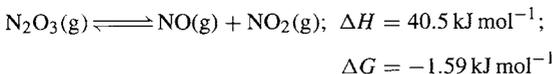
refluxing MeCN, and was shown later to have an M–N–S angle of 172.1° .⁽¹²⁴⁾ More recently $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NS})]$ was made by reacting $\text{Na}[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ with $\text{S}_3\text{N}_3\text{Cl}_3$ and again the NS group was found to adopt an essentially linear coordination with Cr–N–S 176.8° .⁽¹²⁵⁾ See also pp. 721–46 for other sulphur–nitrogen species.

Dinitrogen trioxide, N_2O_3

Pure N_2O_3 can only be obtained at low temperatures because, above its mp (-100.1°C), it dissociates increasingly according to the equilibria:

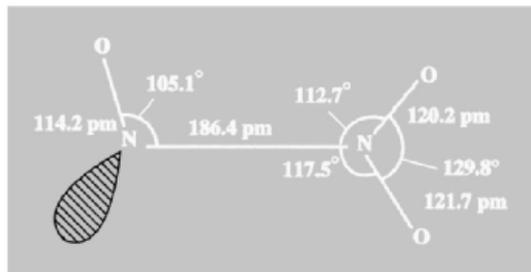


The solid is pale blue; the liquid is an intense blue at low temperatures but the colour fades and becomes greenish due to the presence of NO_2 at higher temperatures. The dissociation also limits the precision with which physical properties of the compound can be determined. At 25°C the dissociative equilibrium in the gas phase is characterized by the following thermodynamic quantities:

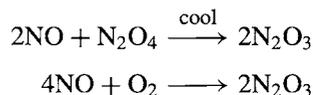


Hence $\Delta S = 139 \text{ J K}^{-1} \text{ mol}^{-1}$ and the equilibrium constant $K(25^\circ\text{C}) = 1.91 \text{ atm}$. Molecules of N_2O_3 are planar with C_s symmetry.

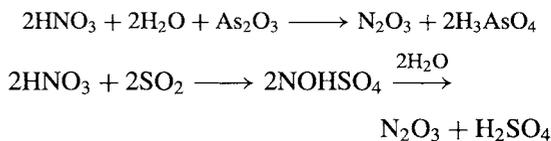
Structural data are in the diagram; these data were obtained from the microwave spectrum of the gas at low temperatures. The long (weak) N–N bond is notable (cf. 145 pm in hydrazine, p. 428). In this N_2O_3 resembles N_2O_4 (p. 455).



N_2O_3 is best prepared simply by condensing equimolar amounts of NO and NO_2 at -20°C or by adding the appropriate amount of O_2 to NO in order to generate the NO_2 *in situ*:

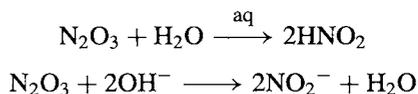


Alternative preparations involve the reduction of 1:1 nitric acid by As_2O_3 at 70° , or the reduction of fuming HNO_3 with SO_2 followed by hydrolysis:

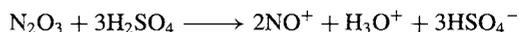


However, these methods do not yield a completely anhydrous product and dehydration can prove difficult.

Studies of the chemical reactivity of N_2O_3 are complicated by its extensive dissociation into NO and NO_2 which are themselves reactive species. With water N_2O_3 acts as the formal anhydride of nitrous acid and in alkaline solution it is converted essentially quantitatively to nitrite:



Reaction with concentrated acids provides a preparative route to nitrosyl salts such as $\text{NO}[\text{HSO}_4]$, $\text{NO}[\text{HSeO}_4]$, $\text{NO}[\text{ClO}_4]$, and $\text{NO}[\text{BF}_4]$, e.g.:



¹²⁴ J. CHATT and J. R. DILWORTH, *J. Chem. Soc., Chem. Commun.*, 508 (1974); crystal structure by M. B. HURSTHOUSE and M. MONTEVALLI quoted by J. CHATT in *Pure Appl. Chem.* **49**, 815–26 (1977). See also M. W. BISHOP, J. CHATT and J. R. DILWORTH, *J. Chem. Soc., Dalton Trans.*, 1–5 (1979).

¹²⁵ T. J. GREENOUGH, B. W. S. KOLTHAMMER, P. LEGZDINS and J. TROTTER, *J. Chem. Soc., Chem. Commun.*, 1036–7 (1978).

Nitrogen dioxide, NO_2 , and dinitrogen tetroxide, N_2O_4

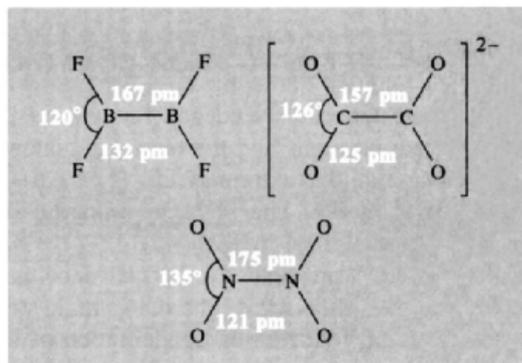
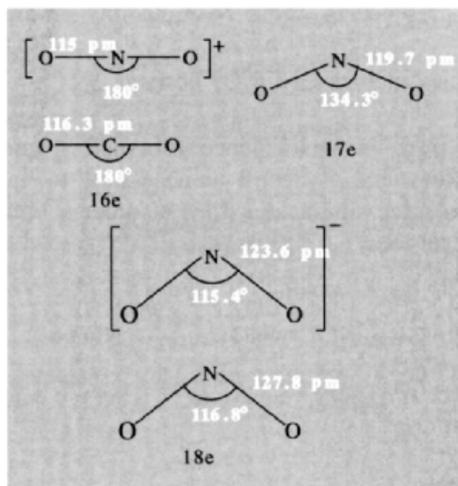
The facile equilibrium $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ makes it impossible to study the pure individual compounds in the temperature range -10° to $+140^\circ$ though the *molecular* properties of each species in the equilibrium mixture can often be determined. At all temperatures below the freezing point (-11.2°) the solid consists entirely of N_2O_4 molecules but the liquid at this temperature has 0.01% NO_2 . At the bp (21.5°C) the liquid contains 0.1% NO_2 but the gas is more extensively dissociated and contains 15.9% NO_2 at this temperature and 99% NO_2 at 135° . The increasing dissociation can readily be followed by a deepening of the brown colour due to NO_2 and an increase in the paramagnetism; the thermodynamic data for the dissociation of $\text{N}_2\text{O}_4(\text{g})$ at 25°C are:

$$\Delta H^\circ 57.20 \text{ kJ mol}^{-1}; \Delta G^\circ 4.77 \text{ kJ mol}^{-1};$$

$$\Delta S^\circ 175.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

The unpaired electron in NO_2 appears to be more localized on the N atom than it is in NO and this may explain the ready dimerization. NO_2 is also readily ionized either by loss of an electron (9.91 eV) to give the nitryl cation NO_2^+ (isoelectronic with CO_2) or by gain of an electron to give the nitrite ion NO_2^- (isoelectronic with O_3). These changes are accompanied by a dramatic diminution in bond angle and an increase in N–O distance as the number of valence electrons increases from 16 to 18 (top diagram).

The structure of N_2O_4 in the gas phase is planar (D_{2h}) with a remarkably long N–N bond, and these features persist in both the monoclinic crystalline form near the mp and the more stable low-temperature cubic form. Data for the monoclinic form are in the lower diagram[†] together with those for the isoelectronic species B_2F_4 and



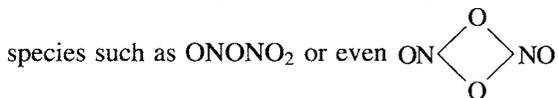
the oxalate ion $\text{C}_2\text{O}_4^{2-}$. The trends in bond angles and terminal bond distances are clear but the long central bond in N_2O_4 is not paralleled in the other 2 molecules where the B–B distance (p. 148) and C–C distance (p. 292) are normal. However, the B–B bond in B_2Cl_4 is also long (175 pm).

In addition to the normal homolytic dissociation of N_2O_4 into 2NO_2 , the molecule sometimes reacts as if by heterolytic fission: thus in media of high dielectric constant the compound often reacts as though dissociated according to the equilibrium $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}^+ + \text{NO}_3^-$ (see p. 457). This has sometimes been taken to imply

(non-planar) molecule $\text{O}_2\text{N}-\text{NO}_2$, and similar experiments at liquid helium temperature (-269°C) have been interpreted in terms of the unstable oxygen-bridged species ONONO_2 .

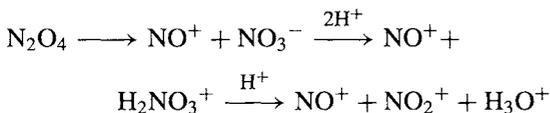
[†] Values for the gas phase are similar but there is a noticeable contraction in the cubic crystalline form (in parentheses). N–N 175 pm (164 pm), N–O 118 pm (117 pm), angle O–N–O 133.7° (126°). In addition, infrared studies on N_2O_4 isolated in a low-temperature matrix at liquid nitrogen temperature (-196°C) have been interpreted in terms of a twisted

the presence in liquid N_2O_4 of oxygen-bridged

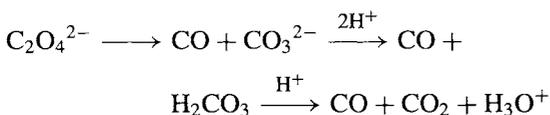


but there is no evidence for such species in solution and it seems unnecessary to invoke them since similar reactions also occur with the oxalate ion:

Thus

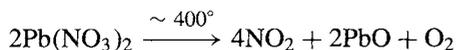


Compare

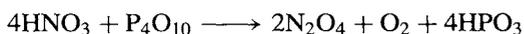


There is no noticeable tendency for pure N_2O_4 to dissociate into ions and the electrical conductivity of the liquid is extremely low ($1.3 \times 10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 0°). The physical properties of N_2O_4 are summarized in Table 11.11.

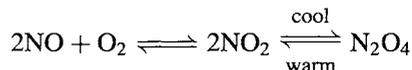
N_2O_4 is best prepared by thermal decomposition of rigorously dried $Pb(NO_3)_2$ in a steel reaction vessel, followed by condensation of the effluent gases and fractional distillation:



Other methods (which are either more tedious or more expensive) include the reaction of nitric acid with SO_2 or P_4O_{10} and the reaction of nitrosyl chloride with $AgNO_3$:

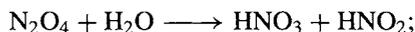


The compound is also formed when NO reacts with oxygen:

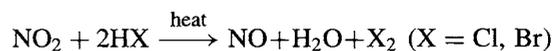


These equilibria limit the temperature range in which reactions of N_2O_4 and NO_2 can be studied since dissociation of N_2O_4 into NO_2 is extensive above room temperature and is virtually complete by 140° whereas decomposition of NO_2 into NO and O_2 becomes significant above 150° and is complete at about 600° .

N_2O_4/NO_2 react with water to form nitric acid (p. 466) and the moist gases are therefore highly corrosive:



The oxidizing action of NO_2 is illustrated by the following:



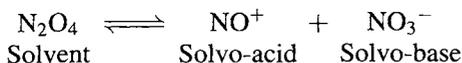
N_2O_4 has been extensively studied as a nonaqueous solvent system⁽¹²⁶⁾ and it is uniquely useful for preparing anhydrous metal nitrates and nitrate complexes (p. 468). Much of the chemistry can be rationalized in terms of a self-ionization equilibrium similar to that observed for

¹²⁶ C. C. ADDISON, in G. JANDER, H. SPANAU and C. C. ADDISON (eds.), *Chemistry in Non-aqueous Ionizing Solvents*, Vol. 3, Part 1, pp. 1–78, Pergamon Press, London, 1967. C. C. ADDISON, *Chem. Rev.* **80**, 21–39 (1980).

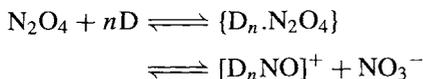
Table 11.11 Some physical properties of N_2O_4

MP/ $^\circ\text{C}$	-11.2	Density(-195°C)/ g cm^{-3}	1.979 (s)
BP/ $^\circ\text{C}$	+21.15	Density(0°C)/ g cm^{-3}	1.4927 (l)
$\Delta H_f^\circ(298 \text{ K})/\text{kJ mol}^{-1}$	9.16	$\eta(0^\circ\text{C})/\text{poise}$	0.527
$\Delta G_f^\circ(298 \text{ K})/\text{kJ mol}^{-1}$	97.83	$\kappa(0^\circ\text{C})/\text{ohm}^{-1} \text{ cm}^{-1}$	1.3×10^{-13}
$S^\circ(298 \text{ K})/\text{J K}^{-1} \text{ mol}^{-1}$	304.2	Dielectric constant ϵ	2.42

liquid ammonia (p. 425):

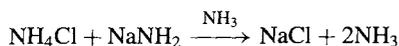
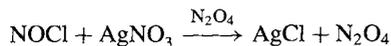


As noted above, there is no physical evidence for this equilibrium in pure N_2O_4 , but the electrical conductivity is considerably enhanced when the liquid is mixed with a solvent of high dielectric constant such as nitromethane ($\epsilon \approx 37$), or with donor solvents (D) such as MeCO_2Et , Et_2O , Me_2SO , or Et_2NNO (diethylnitrosamine):

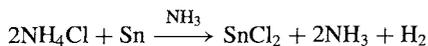
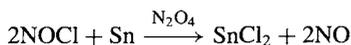


Typical solvent system reactions are summarized below together with the analogous reactions from the liquid ammonia solvent system:

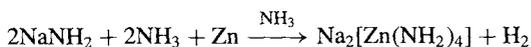
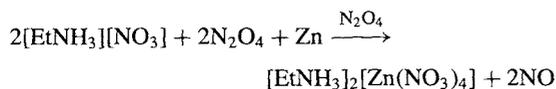
“Neutralization”



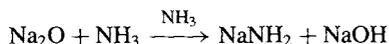
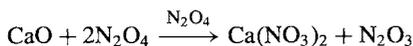
“Acid”



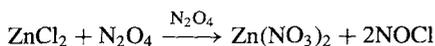
“Base/amphoterism”



“Solvolysis”

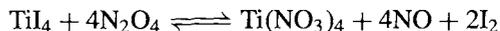


Similarly :

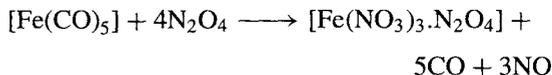
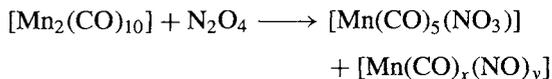


Such reactions provide an excellent route to anhydrous metal nitrates, particularly when metal bromides or iodides are used, since then the nitrosyl halide decomposes and this prevents the possible

formation of nitrosyl compounds, e.g.:



Many carbonyls react similarly, e.g.:



Solvates are frequently formed in these various reactions, e.g.:



Some of these may contain undissociated solvent molecules N_2O_4 but structural studies have revealed that often such “solvates” are actually nitrosonium nitrate-complexes. For example it has been shown⁽¹²⁷⁾ that $[\text{Sc}(\text{NO}_3)_3 \cdot 2\text{N}_2\text{O}_4]$ is, in fact, $[\text{NO}]_2^+[\text{Sc}(\text{NO}_3)_5]^{2-}$. Similarly, X-ray crystallography revealed⁽¹²⁸⁾ that $[\text{Fe}(\text{NO}_3)_3 \cdot 1\frac{1}{2}\text{N}_2\text{O}_4]$ is $[\text{NO}]^+[\text{Fe}(\text{NO}_3)_4]^{2-}[\text{NO}_3]^-$, in which there is a fairly close approach of 3 NO^+ groups to the “uncoordinated” nitrate ion to give a structural unit of stoichiometry $[\text{N}_4\text{O}_6]^{2+}$ (see also p. 472).

In contrast to the wealth of reactions in which N_2O_4 tends to behave as NO^+NO_3^- , there is no evidence for reactions based on the alternative heterolytic dissociation $\text{NO}_2^+\text{NO}_2^-$.⁽¹²⁹⁾ Earlier claims^(129a) to have identified BF_3 adducts such as $[\text{NO}_2]^+[\text{ON}(\text{OBF}_3)]^-$ have been shown to be incorrect and the predominant products of the reaction of BF_3 with N_2O_4 (and also with N_2O_3 and with N_2O_5) are, in fact, NO^+BF_4^- and $\text{NO}_2^+\text{BF}_4^-$.^(129b) This latter compound had

¹²⁷ C. C. ADDISON, A. J. GREENWOOD, M. J. HALEY and N. LOGAN, *J. Chem. Soc., Chem. Commun.*, 580–1 (1978).

¹²⁸ L. J. BLACKWELL, E. K. NUNN and S. C. WALLWORK, *J. Chem. Soc., Dalton Trans.*, 2068–72 (1975).

¹²⁹ C. C. ADDISON, S. ARROWSMITH, M. F. A. DOVE, B. F. G. JOHNSON, N. LOGAN and S. A. WOOD, *Polyhedron* **15**, 781–4 (1996).

^{129a} R. W. SPRAGUE, A. B. GARRETT and H. H. SISLER, *J. Am. Chem. Soc.* **82**, 1059–64 (1960).

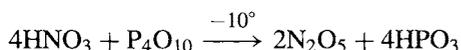
^{129b} J. C. EVANS, H. W. RINN, S. J. KUHN and G. A. OLAH, *Inorg. Chem.* **3**, 857–61 (1964).

earlier (1956) been introduced by G. A. Olah as a powerful, stable nitrating agent in organic chemistry and it has been widely used since then.⁽¹³⁰⁾

N₂O₄ has also been used extensively as a hypogolic oxidizer for hydrazine-based fuels in spacecraft. For example, the Apollo manned lunar landing modules (1969–72) used 5.0 tonnes of liquid N₂O₄ during descent to the lunar surface and 1.5 tonnes during the return ascent, the fuel being a 1:1 mixture of MeNHNH₂ and Me₂NNH₂.

Dinitrogen pentoxide, N₂O₅, and nitrogen trioxide, NO₃

N₂O₅ is the anhydride of nitric acid and is obtained as a highly reactive deliquescent, light-sensitive, colourless, crystalline solid by carefully dehydrating the concentrated acid with P₄O₁₀ at low temperatures:



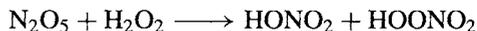
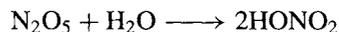
The solid has a vapour pressure of 100 mmHg at 7.5°C and sublimes (1 atm) at 32.4°C, but is thermally unstable both as a solid and as a gas above room temperature. Thermodynamic data at 25°C are:

	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	$\Delta G_f^\circ/\text{kJ mol}^{-1}$	$S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$
N ₂ O ₅ (cryst)	-43.1	113.8	178.2
N ₂ O ₅ (g)	11.3	115.1	355.6

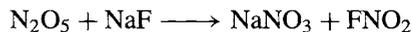
X-ray diffraction studies show that solid N₂O₅ consists of an ionic array of linear NO₂⁺ (N–O 115.4 pm) and planar NO₃[−] (N–O 124 pm). In the gas phase and in solution (CCl₄, CHCl₃, OPCl₃) the compound is molecular; the structure is not well established but may be O₂N–O–NO₂ with a central N–O–N angle close to 180°. The molecular form can also be obtained in the solid phase by rapidly quenching the gas to −180°, but it rapidly reverts to the more stable ionic form

on being warmed to −70°. [cf. ionic and covalent forms of BF₃·2H₂O (p. 198), AlCl₃ (p. 234), PCl₅ (p. 498), etc.]

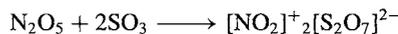
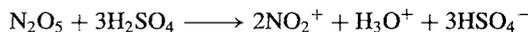
N₂O₅ is readily hydrated to nitric acid and reacts with H₂O₂ to give pernitric acid as a coproduct:



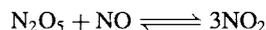
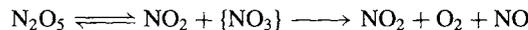
It reacts violently as an oxidizing agent towards many metals, non-metals and organic substances, e.g.:



Like N₂O₄ (p. 457) it dissociates ionically in strong anhydrous acids such as HNO₃, H₃PO₄, H₂SO₄, HSO₃F and HClO₄, and this affords a convenient source of nitronium ions and hence a route to nitronium salts, e.g.:



In the gas phase, N₂O₅ decomposes according to a first-order rate law which can be explained by a dissociative equilibrium followed by rapid reaction according to the scheme



The fugitive, paramagnetic species {NO₃} is also implicated in several other gas-phase reactions involving the oxides of nitrogen and, in the N₂O₅-catalysed decomposition of ozone, its concentration is sufficiently high for its absorption spectrum to be recorded, thereby establishing its integrity as an independent chemical species. Such reactions are the subject of considerable current interest for environmental reasons. NO₃ probably has a symmetrical planar structure (like NO₃[−]) but it has not been isolated as a pure compound.

¹³⁰ G. A. OLAH, R. MALHOTRA and S. C. NARANG, *Nitration: Methods and Mechanisms* VCH Publishers, New York, 1989.