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Modern chemistry of nitrous oxide

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Abstract. Modern trends of the chemistry of nitrous oxide are discussed. Data on its structure, physical properties and reactivity are generalised. The effect of N_2O on the environment and the possibility of its utilisation are considered. Attention is focused on the processes in which the oxidising potential of nitrous oxide can be employed. The bibliography includes 329 references.

I. Introduction

Nitrous oxide was discovered by J Priestley in 1772. After experiments performed by H Davy in 1799, N_2O received the name 'laughing gas' from its action. In the mid-nineteenth century, N_2O assumed importance and found wide application as a soft anaesthetic. Presently, nitrous oxide is used in medicine primarily in mixtures with other more powerful inhalation anaesthetics.[1] Since nitrous oxide is non-toxic and readily soluble in lipophilic media, it finds use in food industry as a foaming agent. Nitrous oxide is one of three compounds containing N–O bonds which were discovered in interstellar space.[2]

In the last two decades, the chemistry of nitrous oxide has been substantially developed. In one aspect or another, N_2O was mentioned in a large body of research. In the present review, the abundant data on nitrous oxide are surveyed. Particular attention is given to studies in which N_2O was described as the reagent. The role of N_2O in the destruction of the ozone layer giving rise to the so-called 'greenhouse' effect is also considered.

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II. Atmospheric nitrous oxide

1. Sources of atmospheric N_2O and its environmental effects

The environmental effects of nitrous oxide have been the subject of much attention of ecologists over the last several decades. This interest is primarily associated with the fact that the role of 'laughing gas' (previously, it had been thought that this gas was quite harmless) in the atmospheric processes is beginning to emerge. It was realised that nitrous oxide plays a role in destruction of the ozone layer and gives rise to the greenhouse effect.

It was demonstrated that the average residence time of nitrous oxide in the lower layers of the atmosphere is about 120 years due to the lack of processes necessary for chemical conversions of N_2O.[3] Nitrous oxide gradually diffuses from the troposphere to the stratosphere, where it decomposes partly through photolysis and partly in reactions with reactive O and $^{\bullet}OH$ species formed upon photolysis.[4]

$$N_2O \xrightarrow{h\nu} N_2 + O(^1D),$$

$$N_2O + O(^1D) \longrightarrow 2\,NO,$$

$$N_2O + O(^1D) \longrightarrow N_2 + O_2,$$

$$N_2O + {}^{\bullet}OH \longrightarrow N_2 + HO_2^{\bullet}.$$

Nitric oxide (NO), in turn, reacts with ozone to form O_2 and NO_2. The latter undergoes disproportionation to give NO and O under the action of solar radiation, this process occurring repeatedly.[5]

Nitrous oxide is the third most abundant minor component of the atmosphere, exceeded in amount only by carbon dioxide and methane. It is believed that these gases along with ozone and Freons are of importance in processes providing thermal balance of the Earth. Their molecules adsorb heat given up by the Earth as infrared radiation resulting finally in a noticeable increase in the temperature of the troposphere and the greenhouse effect.[6, 7] Although the contribution of N_2O to the total greenhouse effect is evaluated at 6%, the 'greenhouse-forming' power of nitrous oxide is approximately 260 times larger than that of carbon dioxide.[4, 5] Taking into account the residence time of nitrous oxide in the atmosphere and the fact that its discharge to the atmosphere from anthropogenic sources cannot be terminated immediately, ecologists have expressed serious concern over the contribution of N_2O to the greenhouse effect.

Analysis of air samples taken from cavities in land ice in Greenland demonstrated that the nitrous oxide content of the

atmosphere remained rather constant ($\sim$ 280 ppb) over the last thousand years.[8] Beginning in the mid-eighteenth century, the growth in industry was accompanied by a progressive increase in the N_2O content in the atmosphere. Presently, the concentration of N_2O in the Northern Hemisphere reaches $\sim$ 314 ppb and continues to increase at a rate of $\sim 0.5-0.9$ ppb per annum. Thus, the nitrous oxide content of the atmosphere increases by 0.2% – 0.3% annually. The same trends are true for the Southern Hemisphere.

Identification of all sources of discharge of nitrous oxide to the atmosphere and quantitative estimation of the contributions of these sources are stubborn problems. For various reasons, the scatter in the data obtained by different researchers is very wide.[4,9] However, the available models are steadily improved with the aim of gaining reliable information on the processes influencing the total balance of emission of N_2O to the atmosphere and its decomposition.[10]

In 1990, emission of nitrous oxide to the atmosphere was $\sim$ 12.7 million tons [11] of which about 35 percent were of anthropogenic origin. Processes of nitrification and denitrification in soils of tropical and temperate regions and in oceanic waters are the major natural contributors of N_2O. It is assumed with a rather low accuracy that these processes are responsible for 45%, 25% and 30% of all natural emission of N_2O, respectively. Heating and power plants,[12,13] motor transport (18%),[14,15] some industrial chemical processes (12%) [16] and agriculture (70%) [17] are recognised to be the major sources of N_2O of anthropogenic origin.

One cannot say that no efforts are being undertaken to decrease the discharge of nitrous oxide to the atmosphere. Thus, the largest world's manufacturers of adipic acid ($\sim$ 5% – 8% of the total anthropogenic emission of N_2O) concluded an agreement [18] and committed themselves to supply plants with special technological cycles and to reduce the amount of N_2O exhausted into the atmosphere by more than 90% by 2000. New catalysts and catalytic processes for decomposition of N_2O are being developed.[19,20] However, agriculture remains the major contributor of nitrous oxide. The amount of nitrous oxide can be reduced by decreasing the use of nitrogen-containing fertilisers and by reducing flooded areas under rice crops where anaerobic processes of N_2O formation occur. However, it is difficult to accomplish this goal because the growth of population generates a need for the solution of food problems, while modern highly productive agricultural crops require the intensive use of nitrogen fertilisers.

Therefore, it was predicted that the N_2O content in the atmosphere will be increased by 0.2% – 0.3% annually in the coming years, as has been observed in recent years.[11,21]

2. Catalytic purification of waste gases from N_2O

Presently, a number of catalytic processes for the neutralisation of pollutants are available and successfully used.[22] Purification of waste gases from N_2O is one of the steps aimed at reducing its discharge to the atmosphere. Apparently, the optimum procedure involves catalytic decomposition of nitrous oxide.

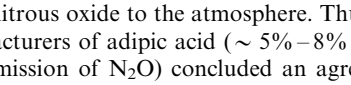
For a long time, investigations in this field were carried out from the standpoint of fundamental science.[19] The available systems often did not satisfy strict requirements imposed upon industrial catalysts for gas purification. More recently, many available catalytic systems have been reinvestigated under 'pseudoindustrial' conditions, *viz*., in the presence of complex gas mixtures, at temperature modes typical of heating furnaces and at high flow rates.[23,24] The world's large manufacturers of adipic acid, for example, DuPont (the catalyst is $CoO-NiO/ZrO_2$), BASF and Asahi (the catalyst is Cu/Al_2O_3), developed new technologies for the utilisation of N_2O.[25,26] However, the available catalytic compositions are far short of optimum. In addition, a wide variety of industrial sources of N_2O emission as well as operating conditions varying over a wide range call for a search for new more perfect catalysts. In addition, it was established that installations used for the neutralisation of NO and NO_2 can serve as sources of nitrous oxide.[25] Denitrification of waste gases in industrial scrubbers is generally performed using selective high-temperature reduction of nitrogen oxides NO_x with ammonia or hydrocarbons in the presence of a catalyst.[27] The conditions and parameters of the reactions of N_2O with reducing agents [RH,[28–33] NH_3 (see Refs 34 and 35) or CO [36–38]] have also been studied extensively. Since the maximum conversions of NO and N_2O into N_2 are achieved at different temperatures, the possibility of the simultaneous removal of these gases is an important criterion for the estimation of the efficiency of catalysts used for the purification of waste gases from nitrogen oxides.[39–41]

It should be mentioned that catalytic procedures for the purification of waste gases from nitrogen oxides are generally more favourable both from the economical standpoint and from the viewpoint of the efficiency of a reduction in the amount of NO_x to the maximum permissible concentrations. The adsorption methods can also be employed for the solution of this problem. Thus Centi *et al.* [42] demonstrated that Ba – ZSM-5 zeolites can be used for the selective removal of nitrous oxide from gas flows containing 0.1% – 0.2% of N_2O, and mixtures enriched with nitrous oxide (5%) can be either utilised as an oxidant or directed to refineries for subsequent decomposition.

III. Structure and properties

1. Structure of the nitrous oxide molecule

Generally, the structure of the nitrous oxide molecule (the symmetry group $C_{\infty v}$) is described by the resonance forms **A** and **B**.



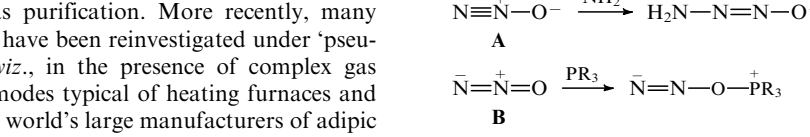
A **B**

It is believed that the *N*-oxide form **A** makes the major contribution to the geometric and electronic structure of the molecule. The total effective charges on the atoms in the form **A** are given below:

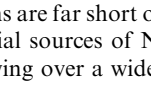
Calculation procedure	q_N	$q_{N(O)}$	q_O	Ref.
CNDO/2	−0.14	0.47	−0.33	43
4-31G	−0.07	0.62	−0.55	44
MP3	−0.11	0.44	−0.33	45

The opposite charge distribution in the resonance forms **A** and **B** accounts for the relatively low dipole moment of the molecule (0.161 D).[46] The N – N bond (1.128 Å) in nitrous oxide is substantially shorter than the standard N = N bond (1.24 Å, MeN = NMe) and is only insignificantly longer than the N ≡ N bond (1.10 Å, N_2). The N – O bond (1.184 Å, N_2O) is quite similar to the standard N = O double bond (1.21 Å, MeN = O).[47] Therefore, the N – N and N – O bond orders in nitrous oxide are estimated at 2.73 and 1.61, respectively.[48]

It is easy to see that the representation of the N_2O molecule by the resonance forms **A** and **B** formally assumes the presence of ambidentate properties, which can be manifested in the reactions of nitrous oxide both with electrophilic [49] and nucleophilic [50] agents.



The zwitterionic resonance forms **A** and **B** can be supplemented with the form **C** (1,3-dipole)

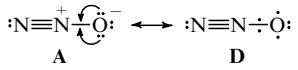


C

which can be involved in cycloaddition.

Data on the formation of stable five-membered rings in the reactions of N_2O with dipolarophiles are lacking. The theoretical possibility of this cycloaddition was discussed.[51,52] Bridson-Jones *et al.*[53] suggested that dihydro-1,2,3-oxadiazoles can be formed as intermediates in high-temperature oxidation of alkenes with nitrous oxide.

It should be noted that the non-classical representation of the nitrous oxide molecule as a biradical **D**[47,54] also allows an adequate description of the behaviour of N_2O in chemical reactions.



A **D**

Within the framework of the molecular orbital method, this description implies that one-electron delocalisation of the $2p\pi_x$ and $2p\pi_y$ orbitals of O^- results in the fact that electrons occupy the π_x and π_y bonding molecular orbitals which form one-electron π_x(NO) and π_y(NO) bonds and weak partial π_x(NN) and π_y(NN) bonds.

2. Brønsted basicity

Based on the data on the equilibrium constants of several tens gas-phase reactions

$$B_1H^+ + B_2 \rightleftharpoons B_2H^+ + B_1$$

the absolute gas-phase basicity scale for a wide range of compounds from N_2 to *tert*-butylamine was proposed.[55] According to this scale, the proton affinity of nitrous oxide (137.8 kcal mol^{-1}) is comparable with those of methane (130.2 kcal mol^{-1}) and carbon monoxide (141.9 kcal mol^{-1}). Olah *et al.*[44] prepared (and characterised) $MeON_2^+$ by the reaction

$$N_2O + MeF \xrightarrow[-80\ ^\circ C]{SO_2F_2,\ SbF_5} MeON_2^+SbF_6^-,$$

However, the authors did not detect the hydroxydiazonium ion $NNOH^+$ in the reaction of N_2O with superacids.

The protonated form of nitrous oxide in the gas phase was detected by IR spectroscopy.[56] The spectral characteristics were not unambiguously assigned to particular isomers, *viz.*, to $NNOH^+$ or ^+HNNO. Calculations[57,58] demonstrated that protonation of the oxygen atom is more favourable than protonation of the nitrogen atom. However, the results of these calculations depend substantially on the electron correlation methods applied.[59]

3. Physical properties

Nitrous oxide is a colourless diamagnetic gas with a weak pleasant odour and sweetish flavour. It is incombustible but can maintain burning. The nitrous oxide molecule is very stable. In the absence of a catalyst at 400–530 °C, thermal decomposition of N_2O is insignificant (0.22%–0.23%)[60]

$$2N_2O \longrightarrow 2N_2 + O_2.$$

The activation energy E_a of this non-adiabatic spin-forbidden process is ~ 59 kcal mol^{-1}.[61]

Nitrous oxide possesses a high critical temperature. At room temperature under high pressure (50.1 atm, 21 °C), it can exist as a liquid and can be stored in steel cylinders. In laboratory conditions, N_2O is generally prepared either by thermal decomposition of ammonium nitrate or by the reaction of potassium nitrosyl sulfate with sulfuric acid.[61] The physical properties of nitrous oxide are given below.[62–64]

Melting point /°C	−90.86
Boiling point /°C	−88.48
Critical pressure /atm	71.7
Critical temperature /°C	36.5
Critical density /g cm^{-3}	0.452
Density of N_2O (liq) at −88.48 °C /g cm^{-3}	1.226
Density of N_2O (g) at 0 °C /mg cm^{-3}	1.997
Enthalpy of formation ($\Delta_fH^0_{298}$) /kcal mol^{-1}	19.6
Free energy of formation ($\Delta_fG^0_{298}$) /kcal mol^{-1}	24.6
Entropy (S^0) /cal K^{-1} mol^{-1}	52.52
Thermal capacity (C^0_p) /cal K^{-1} mol^{-1}	9.19

IV. Decomposition of nitrous oxide

1. Thermal decomposition

Homogeneous thermal decomposition of nitrous oxide is one of the most extensively studied chemical reactions.[65,66] This process is often used as a model for testing new theories and experimental systems[67] and it is also widely employed for the preparation of atomic oxygen $O(^3P)$.[68]

The following most important elementary stages resulting in decomposition of N_2O are distinguished:

$$N_2O + M \longrightarrow N_2 + O + M, \quad (1)$$

$$N_2O + O \longrightarrow N_2 + O_2, \quad (2)$$

$$N_2O + O \longrightarrow NO + NO, \quad (3)$$

$$N_2O + H \longrightarrow N_2 + {}^{\bullet}OH, \quad (4)$$

$$N_2O + {}^{\bullet}OH \longrightarrow N_2 + HO_2^{\bullet}. \quad (5)$$

From the above-listed equations it can be seen that decomposition of nitrous oxide can occur either as a result of collisions with the third body M [reaction (1)] or through secondary reactions with the oxygen atom or with radical species [reactions (2)–(5)]. The nature of the species M and the character and concentrations of the radical species have an essential effect on this process.

In most of the early investigations, the kinetics of decomposition of nitrous oxide was examined in the presence of argon or nitrogen at 850–1300 °C. However, the formation of nitrous oxide in industrial apparatuses used for denitrification of waste gases and in heating and power plants, which are important anthropogenic contributors of N_2O,[9] occurs at moderately high temperatures (600–900 °C) in complex gas mixtures. The necessity of gaining an insight into the kinetics of these processes gave impetus to investigations of thermal decomposition of N_2O at 600–900 °C in the presence of carbon dioxide, water vapour, hydrogen, methane, oxygen and other gases.[69–71]

2. Heterogeneous catalytic decomposition

A search for new alternative oxidants, on the one hand, and the necessity of the environmental protection aimed at reducing industrial discharge of nitrous oxide to the atmosphere, on the other hand, gave impetus to the development of efficient procedures for catalytic decomposition of nitrous oxide. These procedures were devised primarily by large manufacturers of adipic acid. Thus the BASF, Bayer, DuPont and Asahi companies use catalytic systems for decomposition of N_2O in waste gases,[72] whereas the Solutia company employs recirculation of N_2O to the technological cycle and utilises it as an oxidant for the direct preparation of phenol from benzene.[73]

Problems of a search for efficient catalysts of decomposition of nitrous oxide were covered in an excellent review[25] in which the data on decomposition of N_2O with the use of different heterogeneous catalysts published up to 1996 inclusive have been surveyed and analysed. In the cited review, the mechanism and kinetics of decomposition of N_2O were considered, the role of different oxygen forms occurring on the surface of catalysts was discussed and the problem of catalyst poisoning was touched on. However, a body of the published data in this field increases very rapidly and we believe that it is necessary to survey the data published in 1997–2000 (Table 1).[74–106]

The discovery of isothermal oscillation of concentrations of N_2O, N_2 and O_2 upon decomposition of nitrous oxide on the

Table 1. Catalytic systems for decomposition of nitrous oxide.

Catalyst	Support	Ref.
Catalysts fixed on inert supports		
Cu, Co, Ni, K, Mg, Mn, Ba	C	74–79
Rh, Ru	ZrO_2	81, 82
CuO, Ru, RuO_2	Al_2O_3	88–91
Cu	C, Al_2O_3, SiO_2, ZSM-5	92
Rh	USY, NaY, Al_2O_3, ZrO_2, FSM-16, CeO_2, La_2O_3	96–98
CuO, CoO, Fe_2O_3	SiO_2, MgO, CaO	105
Zeolite catalysts		
[Fe], [Al]–ZSM-22		80
Co, Cu, Fe–ZSM-5		83–87
Oxide catalysts		
CaO, MgO		93–95
Ex-hydrotalcites		
Mg, Co, Ti, Al, La, Rh		99–104
Spinels		
$(Mg_xCo_{1-x})Co_2O_4$		106

Cu–ZSM-5 zeolite catalyst [107] was mentioned in a review.[25] Later, a mechanism was proposed according to which the concentrations of the components change in a wave-like fashion due to cyclic oxidation–reduction of active copper(I) centres responsible for decomposition of N_2O.[108–110] Recently, oscillation of nitrous oxide on the Rh/ZrO_2 (Ref. 111) and Fe–ZSM-5 (Ref. 112) catalysts was observed.

3. Photochemical decomposition

Photochemical decomposition of nitrous oxide affords N_2, O_2, NO and NO_2.[113] Spin-forbidden primary processes (6) and (7) occurring under exposure to light ($\lambda \approx 250$ and 200 nm, respectively) are convenient procedures for the preparation of atomic oxygen in investigations of the kinetics of different reactions in the gas phase.[114, 115]

$$N_2O \xrightarrow{h\nu} N_2 + O(^3P) \quad (6)$$

$$N_2O \xrightarrow{h\nu} N_2 + O(^1D) \quad (7)$$

In recent years, considerable attention has been paid to electronic, vibrational and rotational states of both photofragments, *viz*., N_2 and O,[116, 117] with the aim of giving a comprehensive description of N_2O photolysis.

Great interest was also expressed in photochemical reactions of nitrous oxide in the atmosphere [4] because photolytic decomposition of N_2O is the key process in the conversion of nitrous oxide in the stratosphere.

4. Photocatalytic decomposition

Presently, photocatalysis is the most vigorously evolving line of photochemistry,[118, 119] and this method can be successfully used for decomposition of nitrous oxide. Thus photodecomposition of N_2O under irradiation with UV light ($\lambda < 300$ nm) at room temperature readily proceeds on the surfaces of ZnO,[120] TiO_2,[25] Pt/TiO_2 [121] or Cu–ZSM-5.[122] Copper(I) compounds applied to inert supports,[123] Ag, Cu/TiO_2 [124] or ions of different transition metals in zeolite matrices [125] exhibit high catalytic activities. Possible mechanisms of decomposition, in particular, on zeolites ZSM-5, were discussed.[126, 127] Based on the data from IR and UV spectroscopy, it was concluded [127] that the reaction of N_2O with the Ag^+–ZSM-5 system afforded the Ag^+–N_2O complex whose photoactivation resulted in decomposition of nitrous oxide into N_2 and O_2.

Photodissociation of nitrous oxide on heterogeneous catalysts may be very useful not only in denitrification but also in oxidation or destruction of organic compounds. Photocatalytic degradation of salicylic acid [128] in saturated aqueous solutions of N_2O in the presence of ZnO or ZnO/TiO_2 is an example.

V. Chemistry of nitrous oxide

1. Thermodynamical analysis of the use of N_2O as an oxidant

A change in the Gibbs free energy Δ_rG^0 can be used as a criterion for the possibility of a particular reaction occurring. Thus the reactions can take place and proceed spontaneously if Δ_rG^0 (in kcal mol^{-1}) < 0, whereas in the range of 0–10 kcal mol^{-1}, the reactions are unlikely. This situation calls for further investigation. If $\Delta_rG^0 > 10$ kcal mol^{-1}, the reactions cannot proceed; however, special conditions can help in performing these processes. The Δ_rG^0 value at which the reaction under consideration cannot be carried out depends on many factors and the above-mentioned values can be considered only as a very rough estimate.

The thermochemical data for hypothetical and actual reactions of N_2O with the reagents X or HX, which were calculated as differences between the total changes of the enthalpies ($\Delta_fH^0_{298}$) or the Gibbs free energies ($\Delta_fG^0_{298}$) of formation of the final and starting compounds, are given in Tables 2–5.

$$X + N_2O\,(g) \longrightarrow XO + N_2\,(g),$$

$$2XH + 3N_2O\,(g) \longrightarrow 2XO + 3N_2\,(g) + H_2O\,(g).$$

The required thermodynamical properties of individual compounds were taken from handbooks.[129–133] It should be emphasised once again that the data in Tables 2–5 serve only as a qualitative estimate of the possibility for the reaction to occur. In addition, the above-mentioned data should be compared with each other with caution because the compounds exist in different

Table 2. Changes in the Gibbs free energy of the reactions of nitrous oxide with inorganic compounds.

Substrate (X or HX)	Reaction product (XO)	$\Delta_rH^\circ_{298}$	$\Delta_rG^\circ_{298}$
PCl_3 (g)	$POCl_3$ (g)	−88	−87
CO (g)	CO_2 (g)	−89	−86
SO_2 (g)	SO_3 (g)	−43	−42
NH_3 (g)	NH_2OH (sol)	−34	–
NH_3 (g)	N_2 (g)	−210	−230
H_2O (g)	H_2O_2 (g)	6	5
H_2 (g)	H_2O (g)	−77	−80
Cu (sol)	CuO (sol)	−57	−55

Note. Hereinafter, the values are given in kcal mol^{-1}.

Table 3. Changes in the Gibbs free energy of the reactions of nitrous oxide with some classes of organic compounds.

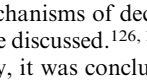
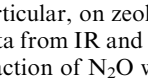
Substrate (X)	Reaction product (XO)	$\Delta_rH^\circ_{298}$	$\Delta_rG^\circ_{298}$
PhSH (liq)	PhSSPh (liq)	−57	–
Me_2S (g)	Me_2SO (liq)	−58	−50
Me_2SO (liq)	Me_2SO_2 (sol)	−80	−73
MeNC (g)	MeNCO (liq)	−77	–
PhN=NPh (sol)	PhN(O)=NPh (sol)	−42	–
		−35	−47

Table 4. Changes in the Gibbs free energy of the reactions of nitrous oxide with aliphatic and aromatic hydrocarbons.

Substrate (X)	Reaction product (XO)	$\Delta_r H^\circ_{298}$	$\Delta_r G^\circ_{298}$
CH_4 (g)	MeOH (g)	−50	−51
MeOH (g)	HCOH (g)	−57	−68
HCOH (g)	HCO_2H (g)	−82	−81
n-C_3H_8 (g)	MeCH(OH)Me (g)	−61	−61
MeCH(OH)Me (g)	$Me_2C(O)$ (g)	−63	−74
Me_3CH (g)	Me_3COH (liq)	−73	−64
Me_3COH (liq)	Me_3COOH (liq)	−4	–
$H_2C=CH_2$ (g)	(g)	−47	−54
$CH_2=CHMe$ (g)	$CH_2=CHCH_2OH$ (g)	−56	−57
$CH_2=CHCH_2OH$ (g)	$CH_2=CHCHO$ (g)	−64	−73
$CH_2=CHCHO$ (g)	$CH_2=CHCO_2H$ (g)	−82	−82
PhH (g)	PhOH (g)	−62	−64
PhMe (liq)	$PhCH_2OH$ (liq)	−61	−59
$PhCH_2OH$ (liq)	PhCHO (liq)	−76	–
PhCHO (liq)	$PhCO_2H$ (sol)	−94	–
$PhCO_2H$ (sol)	$PhCO_3H$ (sol)	−15	–
PhEt (liq)	PhCOMe (liq)	−128	−137
 (liq)	 (sol)	−82	–
 (liq)	 (liq)	−59	–

Table 5. Changes in the Gibbs free energy of some reactions involving nitrous oxide.

Reaction type	$\Delta_r H^\circ_{298}$	$\Delta_r G^\circ_{298}$
$4\,Na\,(sol) + 3\,N_2O\,(g) + NH_3\,(g) \rightarrow$ $\rightarrow NaN_3\,(sol) + 3\,NaOH\,(sol) + 2\,N_2\,(g)$	−349	−322
$2\,NaNH_2\,(sol) + N_2O\,(g) \rightarrow$ $\rightarrow NaN_3\,(sol) + NaOH\,(sol) + NH_3\,(g)$	−71	−70
$C_6H_{11}NH_2\,(g) + N_2O\,(g) \rightarrow C_6H_{11}N_3\,(liq) + H_2O\,(liq)$	−27	–
$2\,NH_3\,(sol) + N_2O\,(g) \rightarrow NH_4N_3\,(sol) + H_2O\,(liq)$	−38	−8
$2\,Na_2O\,(sol) + N_2O\,(g) + NH_3\,(g) \rightarrow$ $\rightarrow NaN_3\,(sol) + 3\,NaOH\,(sol)$	−112	–

physical states and the determined Gibbs energies and enthalpies of the initial and final compounds may be inexact.

Therefore, N_2O is potentially a powerful oxidant. However, only the data on high-temperature oxidation of organic substrates on heterogeneous catalysts and several examples of oxidation of some substrates in homogeneous reactions catalysed by transition-metal complexes are available in the literature. Evidently, this inertness is associated with the high activation energy of decomposition of nitrous oxide. Apparently, this problem can be solved by searching for suitable catalysts.

2. The use of N_2O in oxidative catalysis

Considerable progress has been achieved in oxidative catalysis over the latter part of the twentieth century;[134] however, the advances in oxidative hydroxylation of paraffins and aromatic compounds are still poor. Generally, the reactions using atmospheric or molecular oxygen as an oxidant proceed with low selectivity (sometimes these reactions lead to complete oxidation of the substrate). Presently, several major approaches to the solution of this problem are available, *viz*., the employment of membrane-type reactors,[135, 136] the separate performance of reduction and reoxidation of catalyst's surface (two-step process) [137] or the use of alternative oxidants. In the latter case, major hopes are placed on the use of hydrogen peroxide on titanium silicate catalysts [138] and nitrous oxide on ZSM-5 zeolite catalysts.[139]

Two main lines of investigation, *viz*., selective oxidation of aliphatic (aromatic) hydrocarbons and oxidative condensation of lower alkanes, were mentioned in reviews [139, 140] devoted to the employment of N_2O as an oxidant under conditions of heterogeneous catalysis. However, in spite of a large number of studies,[141–151] the latter reaction is, in Krylov's opinion,[152] substantially less useful than other oxidative conversions of hydrocarbons. Actually, direct oxidation reactions of benzene to phenol or of methane to methanol are of importance. Phenol is still prepared by the oxidation of cumene, and methanol is prepared by the conversion of the synthesis gas. A multitude of catalytic systems, including those involving N_2O as an oxidant, *viz*., various metal oxides (mixed solid solutions doped with ions of other metals fixed on inert supports), heteropolyacids and their salts, zeolites, *etc*., were examined in direct oxidation reactions of benzene and methane.[139, 140] Some catalysts of hydroxylation of methane and benzene with nitrous oxide are listed in Table 6. However, attempts to perform the selective conversion of methane to methanol failed.

Table 6. Catalysts of oxidative hydroxylation with the use of nitrous oxide.

Hydrocarbon	Catalytic system	Ref.
Benzene	Fe–Si, $FePO_4$, H–Ga–FER	153, 154
	H, Na, H–[Al], Fe–ZSM-5	156–159
Methane	Fe–Si, $FePO_4$, H–Ga–FER	155
	H, Na, H–[Al], Fe–ZSM-5	160–162
	Sr- or Ca-hydroxyapatites	163, 164
	Mo/SiO_2	165
	12-phosphomolybdic acid	166

The major progress has been achieved in performing the oxidation of benzene to phenol.[167] A new procedure for the synthesis of phenol, which is based on the use of Fe-containing ZSM-5 zeolites and is characterised by high selectivity with respect to both phenol (97%–98%) and nitrous oxide (85%), was developed by researchers from the G K Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences in cooperation with the Solutia company (USA). Successful tests of a pilot plant were performed and the construction of the industrial plant (Pensacola, Florida) rated at 140 thousand tons of phenol per annum is being brought to completion.[168] It should be noted that the results of many investigations in this field were covered by patents.[169–176]

The nature of high catalytic activity of zeolites in oxidation of benzene is the matter of vivid debates. Presently, two major hypotheses are available. One of them is based on a conventional view of zeolites as acid catalysts whose activity is associated with Lewis [156, 159, 177] and (or) Brønsted [178, 179] acidic centres. However, a special investigation [180] did not confirm the hypothesis based on the concept of Brønsted centres.

The second hypothesis was proposed by Panov *et al*.[139, 181] These authors believed that the interaction of N_2O with the surface of Fe-ZSM-5 zeolites afforded a special form of surface oxygen arbitrarily called α-oxygen. In its properties, α-oxygen differs substantially from the known surface forms of oxygen.[182, 183] α-Oxygen cannot be formed upon adsorption of molecular O_2. It was assumed that α-oxygen resembles somewhat active oxygen of monooxygenases for which hydroxylation of C–H bonds is a typical reaction. Quantum-chemical calculations

of the thermodynamical and geometric parameters of the formation of α-oxygen and its successive reactions with benzene or methane were performed.[184, 185]

It was demonstrated[162] that CH_4 reacted virtually quantitatively with the α-form of oxygen, which arose as a result of decomposition of N_2O on Fe-ZSM-5 zeolite, at room temperature. However, the resulting methanol was strongly bound to the zeolite surface and its desorption into the gas phase did not occur. An increase in the temperature to 250–300 °C led to vigorous CO evolution due to secondary conversion of the product.

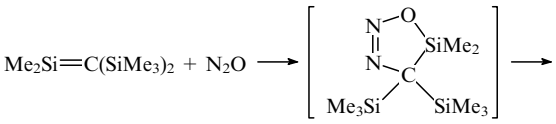
A search for possible catalysts of selective oxidation of hydrocarbons is not restricted to zeolites. Different research groups made efforts to search for a means of activation of C–H bonds.[186] Wang *et al.*[187] succeeded in performing oxidative carbonylation of methane on $Rh/FePO_4$ at 300–400 °C in the presence of CO and nitrous oxide to form MeOH, $MeCO_2H$ and $MeCO_2Me$. Partial oxidation of methane with nitrous oxide under conditions of plasma discharge[188] gave rise to HCHO and MeOH in a total yield of 10%, which is comparable with the results obtained with the use of the best catalytic systems.

On the whole, the problem of direct oxidation of methane to form methanol, in spite of efforts made, is still far from solution.

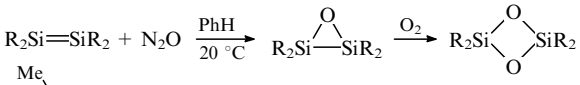
3. Oxidation reactions involving N_2O

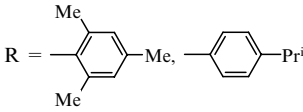
As mentioned above, nitrous oxide is a potentially strong oxidant, but it is very inert for kinetic reasons. Under mild conditions, N_2O reacts only with highly reactive compounds, such as organoboranes,[189] silaethenes[190] or disilenes.[191]

$$BEt_3 + N_2O \xrightarrow[-15\ ^\circ C]{C_6H_{14}} N_2 + (Et_2B)_2O + C_2H_4 + H_2O$$

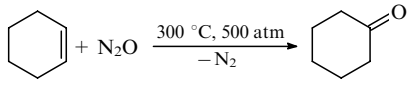


$$\longrightarrow (Me_2SiO)_n + (Me_3Si)_2CN_2$$



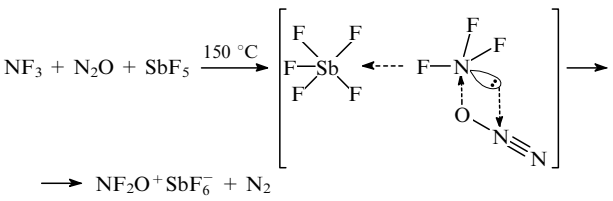


In the absence of a catalyst, N_2O does not react with alkanes, arenes, amines, esters and aliphatic alcohols even at 200–300 °C and 100–500 atm.[53] Under these conditions, alkenes and alkynes form predominantly carbonyl compounds.[192, 193]



The reactions of nitrous oxide with a solution of triethyl phosphite or cyclohexyl isocyanide in benzene (20 atm, 130 °C) afforded triethyl phosphate (80%) or cyclohexyl isocyanate (20%), respectively.[194] A series of oxides of tertiary phosphines were prepared in quantitative yields[195] with the use of nitrous oxide in the supercritical state (100–140 atm, 60–100 °C).

The reaction of N_2O with nitrogen trifluoride in the presence of an excess of SbF_5 gave rise to $NF_2O^+Sb_2F_{11}^-$ whose vacuum pyrolysis afforded NF_3O.[196] Until recently, procedures for the preparation of NF_3O by direct chemical oxo transfer from an O-donor to NF_3 were lacking.



Oxidation of aqueous solutions of alcohols, amines and ethers with nitrous oxide in the presence of Pt or Pd black proceeds according to a radical mechanism.[197] It is assumed that reductive decomposition of N_2O adsorbed on platinum gives rise to N_2 and the $Pt(^{\bullet}OH)$ radicals, which are strong electrophilic oxidants.

$$Me_2CHOH + Pt(^{\bullet}OH) \longrightarrow Me_2\dot{C}OH + H_2O + Pt,$$

$$Pt(N_2O) + Me_2\dot{C}OH \longrightarrow N_2 + Me_2CO + Pt(^{\bullet}OH).$$

On the whole, activation of N_2O is generally a necessary condition for its involvement in oxidation as the oxo donor.

4. Reactions with nucleophilic reagents

The reactions of N_2O with melts of amides of alkali metals and alkaline-earth metals giving rise to the corresponding azides are among the most important reactions of nitrous oxide with nucleophilic reagents.[50] Since sodium azide is rather stable, it serves as the starting compound for the preparation of other azides, and this reaction provides the basis for the industrial production of NaN_3.[198]

$$2NaNH_2 + N_2O \longrightarrow NaN_3 + NaOH + NH_3.$$

Sodium azide is also formed in the reaction of N_2O either with Na in liquid ammonia

$$4Na + 3N_2O + NH_3 \longrightarrow NaN_3 + 3NaOH + 2N_2,$$

or with sodium oxide[61]

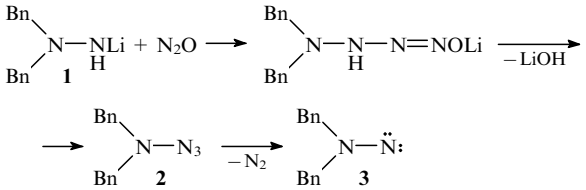
$$2Na_2O + N_2O + NH_3 \xrightarrow{110-190\ ^\circ C} NaN_3 + 3NaOH.$$

The reaction of N_2O with ammonia over the $Ni-Al_2O_3$ catalyst afforded ammonium azide[63]

$$2NH_3 + N_2O \xrightarrow{Ni-Al_2O_3} NH_4N_3 + H_2O.$$

Diazo transfer from nitrous oxide to anions of different anilines was carried out (2–5 atm, 20 °C)[199] and the corresponding aryl azides were isolated (10%–35%).

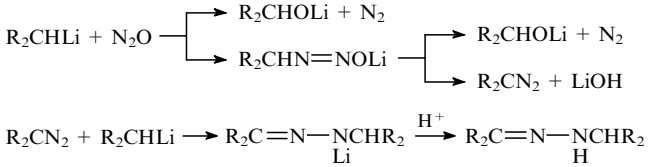
The reaction of N_2O with the monolithium derivative of 1,1-dibenzylhydrazine (**1**) proceeded successively through the formation of *N*-azidoamine **2** and *N*-nitrene **3**.[200]



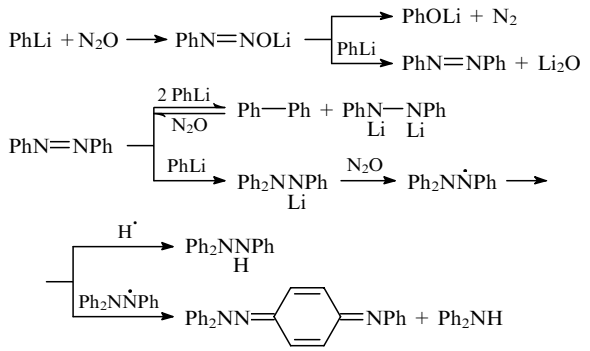
1,2-Diphenylethane (12%) and *N*,*N*-dibenzylbenzalhydrazone (11%) were identified as the major products of the above reaction.

The reactions of N_2O with phosphorus ylide $Ph_3P^+CH_2^-$ (see Ref. 201) or with MeLi[202] gave rise to diazomethane (in 25% or 70% yields, respectively). It should be noted that, with rare exceptions, the reactions of nitrous oxide with anions of organolithium compounds afforded mixtures of *N*- and *O*-products due to the ambidentate character of the former. In addition, the possibility of direct oxidation of organometallic compounds with nitrous oxide must not be ruled out. Based on the results of investigations into the reactions of N_2O with different organolithium compounds, two pathways were proposed.

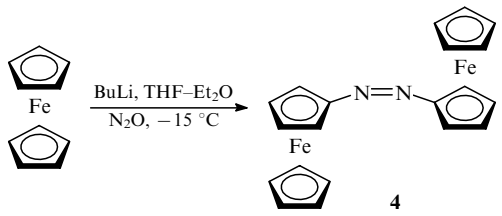
Pathway *a* (see Ref. 203)



Pathway *b* (see Refs 204, 205)



To our knowledge, the procedure for the preparation of diazoferrocene (**4**) (the yield was 25%) developed by Nesmeyanov *et al.*[206] is the only example of the successful application (from the synthetic standpoint) of diazo transfer involving nitrous oxide.



4

Recently, this procedure was used for the preparation of N=N-bonded ferrocene oligomers.[207, 208]

Grignard reagents, unlike organolithium compounds, do not react with nitrous oxide.[203] However, it was demonstrated [209] that the reaction of PhMgBr with N_2O in the presence of CuCl (10 mol.%) afforded small amounts of PhN=NPh (2%) and Ph_2NH (1%). Previously, it has been found [210] that organocalcium analogues of Grignard reagents, for example, PhCaI, reacted with N_2O to yield azobenzene (8%), biphenyl (10%) and traces of benzidine, phenol and hydrazobenzene.

The potential of this reaction as a new procedure for the formation of C–N bonds was examined. [211] It appeared that the yields and the ratio of the reaction products depend substantially on the solvent and the type of substitution in the benzene ring. The maximum yield of azobenzene (60%) was achieved in dimethoxyethane. However, substantial amounts of biphenyl obtained as a by-product impair the synthetic significance of this reaction. The reaction of N_2O with Ph_2Ca afforded azobenzene as the major product (10%).[211] This provides evidence that PhN=NPh can be formed by the direct insertion of N_2O at the R–M–R bond, and not just by the reaction of diazotate R–N=N–OM with the second R–M molecule, as has been suggested previously.[210]

5. Reactions with metal-complex compounds

Nitrous oxide can act as the oxo donor in reactions with metal-complex compounds. The pioneering studies in this field were performed by Bottomley *et al.*[212–218] The authors used N_2O as an oxidant for the synthesis of a series of oxometallocenes with terminal and(or) bridging oxygen atoms, such as oxocyclopentadienyl derivatives of titanium,[213, 214] chromium [215, 216] and vanadium.[217, 218]

Generally, the reactions of low-valence cyclopentadienyl derivatives of transition metals with N_2O afford oxometallocenes containing the central metal atom in an intermediate oxidation state, whereas the reactions with O_2 give rise to oxo clusters containing the metal atoms in the highest oxidation state.[212] Thus oxidation of dicyclopentadienylchromium with oxygen [212] or nitrous oxide [216] afforded two different derivatives, *viz.*, **5** and **6**, respectively.

$$2(\eta\text{-}C_5Me_5)_2Cr + 2O_2 \longrightarrow [(\eta\text{-}C_5Me_5)Cr(O)(\mu\text{-}O)]_2 + (C_5Me_5)_2,$$

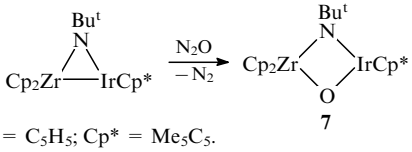
5

$$4(\eta\text{-}C_5Me_5)_2Cr + 4N_2O \longrightarrow [(\eta\text{-}C_5Me_5)Cr(\mu_3\text{-}O)]_4 + 4N_2 + 2(C_5Me_5)_2.$$

6

From Bottomley's standpoint [212] this fact cannot be explained only by thermodynamical reasons [the energy of the N–O (D^0_{298}) bond in N_2O is ~ 40 kcal mol^{-1} and the energy of the O–O bond in O_2 is 119 kcal mol^{-1}].[133] The difference in the structures of oxometallocenes should be determined by the reaction mechanisms, which are poorly understood so far because of their complexity. The reactions of titanocene and vanadocene [219] with nitrous oxide proceeded through the formation of the monomers $[(\eta\text{-}C_5Me_5)_2]M(O)$ (M = Ti or V) whose decomposition afforded the oxo clusters $[(\eta\text{-}C_5Me_5)M_4(\mu\text{-}O)_6]$.

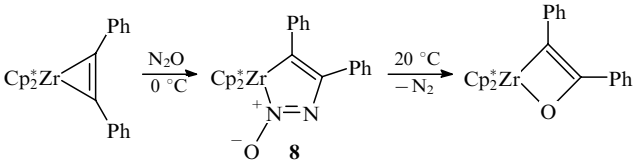
More recently, many researchers used nitrous oxide along with conventional oxo donors (PyO, $OPPh_3$, Me_2SO or O_2) for the preparation of different terminal (bridging) oxo metal complexes. Thus the reactions of N_2O with the tetraaza[14]annulene–Sn(II) complex,[220] $U(OC_6H_3Bu^t_2\text{-}2,6)_3$ (see Ref. 221) and $V[(Me_3SiNCH_2CH_2)_3N]$ [222] were reported. Cyclopentadienyl derivatives of uranium,[223] samarium,[224] zirconium [225, 226] and hafnium [227] also reacted with nitrous oxide to give oxo compounds. The heterobinuclear zirconium–iridium oxo complex **7** was prepared.[228]



7

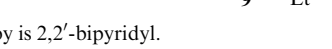
Cp = C_5H_5; Cp* = Me_5C_5.

The reactions of N_2O with metal complexes can be accompanied by insertion of the former at the $(L_n)M-R$ bond. Generally, these reactions afford compounds of the $(L_n)MOR$ type as the final products. However, intermediate complexes **8** containing the nitrous oxide molecule were isolated and characterised in the case of titano- [229] and zirconocene [230, 231] systems.



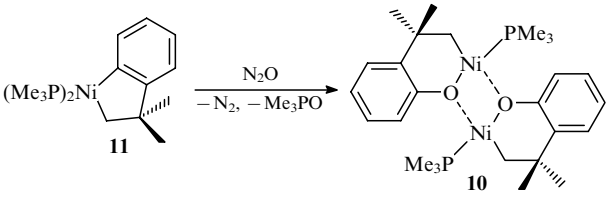
8

Nickel compounds reacted with N_2O to form stable alkyl(aryl)oxy complexes **9** and **10**.[232–234]



9

bipy is 2,2′-bipyridyl.

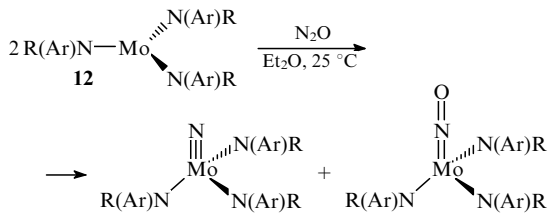


11 **10**

It was proposed [232] that the reaction with nickel complex **11** proceeded *via* intermediates analogous to the zirconium complexes **8**.

The insertion of N_2O at the $(L_n)M-R$ bond giving rise to the $(L_n)MOR$ compounds was described for the complexes of Hf [235] and Ru.[236, 237]

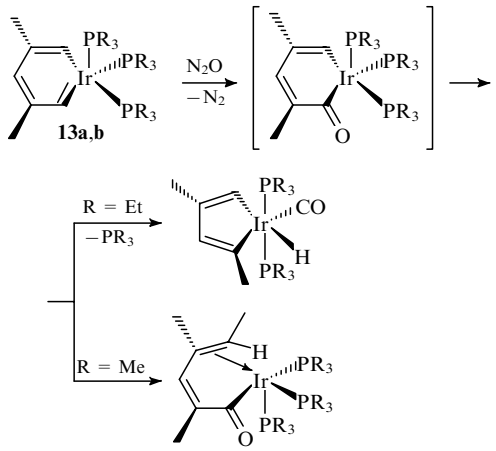
The reactions of nitrous oxide with some metal complexes proceed according to unique mechanisms. Thus the molybdenum complex **12** is the only known metal complex, which can cleave the N–N bond in the N_2O molecule.[238]



R = $C(CD_3)_2Me$; Ar = $C_6H_3Me_2$-3,5.

Based on the results of calculations, it was suggested [239] that the reactions of this complex with N_2O and N_2 proceed by different mechanisms, *viz*., by bimolecular and monomolecular mechanisms in the cases of nitrous oxide and N_2, respectively.

Two different complexes were obtained in the reactions of iridabenzenes **13a**,**b**, which differ by the substituents in the phosphine ligands.[240]



R = Et (**a**), Me (**b**).

It was found [241] that the reactions of the $[Cr(OCP)Li_2(THF)_4]$ complex (OCP is octaalkylcalix[4]pyrrole) with N_2O gave rise to two different oxygen-containing products depending on the solvent used.

6. Metal-complex catalysis of oxo transfer

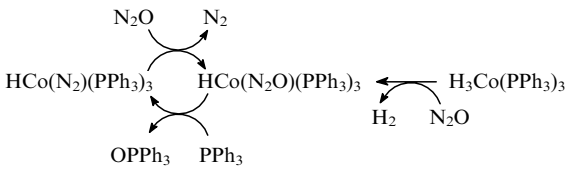
Apparently, the high activation energy of decomposition of N_2O (E_a = 59 kcal mol^{-1}) [61]

$$N_2O\,(g) \longrightarrow N_2\,(g) + O\,(g)\,(^1D), \quad \Delta H^\circ = 85 \text{ kcal mol}^{-1},$$

$$N_2O\,(g) \longrightarrow N_2\,(g) + O\,(g)\,(^3P), \quad \Delta H^\circ = 40 \text{ kcal mol}^{-1},$$

is the only factor that prevents the wide use of nitrous oxide as an oxo donor. Powerful inexpensive nitrous oxide, which can be readily removed from the reaction medium and does not introduce impurities, could be a valuable oxidant. A search for suitable catalysts of N_2O decomposition seems to be the most promising way of solving this problem. Oxo transfer from the reagent to the substrate under the action of metal-complex catalysts is used in various reactions.[242] Acyl(alkyl) peroxides, molecular oxygen, amine *N*-oxides, hydrogen peroxide and aryliodoso compounds are most popular oxo donors. Attempts to use nitrous oxide have also been undertaken, but no noticeable success has been achieved. Generally, elimination of the O atom from N_2O either gives rise to oxo derivatives of complexes which cannot participate in the catalytic cycle for various reasons, or leads to the oxidation of ligands involved in the coordination sphere about the metal atom.

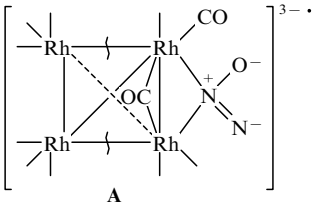
Thus the use of N_2O in the catalytic cycle of oxidation of PPh_3 to form Ph_3PO in the presence of $HCo(N_2)(PPh_3)_3$ was reported.[243] The following reaction scheme was proposed:



Oxidation of carbon monoxide is catalysed by carbonyl complexes of Rh,[244] Ru, Os or Fe.[245]

$$N_2O + CO \xrightarrow{cat} N_2 + CO_2.$$

It was suggested [245] that the reactions in the [Rh]–CO–N_2O and [Fe]–CO–N_2O systems proceeded through different mechanisms. In the case of rhodium complexes, the catalytic cycle involves one-electron transfer from $[Rh(CO)]^-$ to N_2O yielding $N_2O^{-\bullet}$, its capture by the $[Rh_4(CO)_{11}]^{2-}$ anion and subsequent elimination of N_2 and CO_2 (the fragment **A** of the resulting cluster **14** is shown).



A

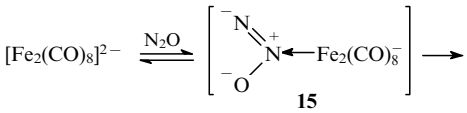
$$[Rh(CO)_4] + N_2O \rightleftharpoons [Rh(CO)_4]^\bullet + N_2O^{-\bullet}$$

$$[Rh_4(CO)_{11}]^{2-} + N_2O^{-\bullet} \longrightarrow [Rh_4(CO)_{11}(N_2O)]^{3-\bullet} \longrightarrow$$

14

$$\longrightarrow [Rh_4(CO)_{10}]^{3-\bullet} + N_2 + CO_2$$

In the presence of iron carbonyls, the nucleophilic attack of N_2O on the reactive intermediates occurs giving rise to an intermediate adduct **15**.

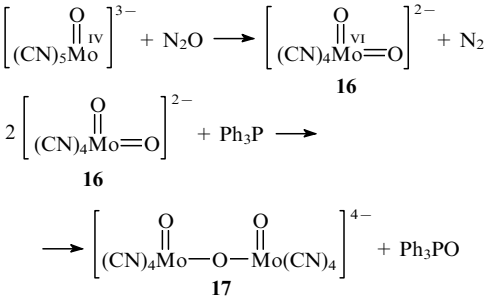


15

$$\longrightarrow [Fe_2(CO)_7]^{2-} + CO_2 + N_2$$

It should be mentioned that molecules which are incorporated into complexes and can regenerate these complexes in the catalytic cycle serve as substrates in the above-considered oxidation reactions involving N_2O. These reactions are not versatile, which impairs their practical significance. Oxidation of CO [246, 247] and PR_3,[248] which are incorporated into metal complexes, with nitrous oxide beyond the catalytic cycle is also documented. The reactions of nitrous oxide with cyclopentadienyl complexes of cobalt at 130 °C resulted in their decomposition to form the corresponding furans and but-2-ene-1,4-dials.[249]

Oxo transfer from N_2O to triphenylphosphine in the presence of $[(CN)_5Mo(O)](PPh_4)_3$ proceeded through the formation of $[(CN)_4Mo(O)_2]^{2-}$ (**16**), the latter serving as an oxidant.[250]



16

17

However, the reaction of the dioxo complex **16** with the substrate afforded compound **17**, which cannot be involved in subsequent reactions, and these reaction cannot be performed in the catalytic mode. Triphenylphosphine was oxidised with nitrous oxide in an autoclave at 80 °C in the presence of phthalocyanine complexes of Al and Cu.[251]

In the studies cited, the possibility of the use of N_2O as the oxo donor in reactions catalysed by metal complexes was merely mentioned. However, a series of investigations in which N_2O was used in the catalytic cycle were published in recent years. Thus it was demonstrated [252] that Ru(II)(TMP)$(THF)_2$ (TMP is tetramesitylporphyrin) reacted with nitrous oxide under mild conditions. The reaction of the resulting complex, *viz.*, of *trans*-Ru(VI)$(O)_2$(TMP), with styrene afforded finally the starting Ru(II) complex and oxirane, thus closing the catalytic cycle. Yamada *et al.*[253] examined the possibility of activation of nitrous oxide with some low-valent transition-metal complexes. Oxidation of PPh_3 was used as the model reaction in the presence of acetylacetonates of the corresponding metals as precatalysts. It was found that Co- and Ni-containing compounds exhibit high activities. The reactions were carried out in the presence of 20 mol.% of metal acetylacetonate and 40 mol.% of diisobutylaluminium hydride under atmospheric pressure of N_2O.

$$Ph_3P \xrightarrow[N_2O,\ 20\ ^\circ C,\ PhMe]{M(acac)_n,\ Bu^i_2AlH} Ph_3PO$$

$M(acac)_n$	$Co(acac)_2$	$Ru(acac)_3$	$Fe(acac)_3$	$Pd(acac)_2$	$Ni(acac)_2$
Yield Ph_3PO (%)	98	43	18	0	89

VI. Applied aspects of the chemistry of nitrous oxide

1. Reduction in protic media

Reduction of nitrous oxide with a copper-containing enzyme, *viz.*, N_2O reductase, is one of the stages of microbiological denitrification [254]

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2,$$

which, in turn, together with nitrogen fixation and nitrification comprise the global biogeochemical cycle of nitrogen in nature. At the same time, nitrous oxide can serve as a substrate both for natural nitrogenases [255,256] and for synthetic protic nitrogen-fixing systems.[257]

$$N_2O + 2e^- + 2H^+ \longrightarrow N_2 + H_2O.$$

It was demonstrated [258] that N_2O reacts also with aprotic synthetic nitrogen-fixing compositions.

$$Li-Me_3SiCl-MCl_n + N_2O \xrightarrow[-LiCl]{THF,\ 20\ ^\circ C,\ 24\ h} \longrightarrow [M{-}N(SiMe_3)_n] + (Me_3Si)_3N + Me_3SiOSiMe_3$$

M = Cr, Fe, Co, Ti.

A number of other metal-containing enzymes (CO dehydrogenase [259] and methionine synthetase [260]) also react with nitrous oxide.

Aqueous solutions of strong reductants, such as $CrCl_2$, can also reduce nitrous oxide [261] although this reduction proceeds very slowly. The rate constant of this reaction increases more than 10^8 times if nitrous oxide is present as a ligand in the $[Ru(NH_3)_5(N_2O)]^{2+}$ complex.[262] This complex, which was isolated in its individual state as salts with PF_6^- or BF_4^-,[263] is presently the only known stable metal complex containing N_2O as a ligand. The mode of coordination of nitrous oxide in this complex is not finally established;[264] however, according to calculations,[265] the Ru–NNO mode of bonding is preferential.

The reactions of N_2O with solutions of some transition-metal compounds were investigated.[266] In particular, it was demonstrated that the reduction of N_2O in aqueous solutions with potassium borohydride was catalysed by cobalt complexes $Co(bipy)_3(ClO_4)_3$ and $Co(DMG)_2PyCl$ (DMG is dimethylglyoxime) and by vitamin B_{12}.

$$Co(I) + N_2O \longrightarrow Co(II) + N_2.$$

In the absence of a reductant, vitamin B_{12} is oxidised by N_2O according to the following scheme

$$Cob(I)alamin + N_2O + H_2O \longrightarrow Cob(III)alamin + N_2 + 2OH^-,$$

$$Cob(I)alamin + Cob(III)alamin \longrightarrow 2Cob(II)alamin.$$

The discovery of this reaction, which proceeds both *in vitro* and *in vivo*, was of importance for anaesthetics and hematology.[267]

Tetraaza[14]annulene compounds of Ni(I) and Cu(I) also proved to be capable of reducing N_2O in the two-electron mode.[268] The Ni(II)Ann complex (Ann is tetraaza[14]annulene) was subsequently used as a catalyst of electrochemical reduction of nitrous oxide and showed high efficiency and chemical stability.[269]

Reduction of N_2O in aqueous solutions is a thermodynamically favourable process. However, in most cases the reactions in the absence of a catalyst proceed very slowly for kinetic reasons.

2. Electrocatalytic reduction

Presently, electrochemical processes are successfully used both in the synthesis of a great variety of compounds and in environmentally safe technological processes.[270,271] It is known that N_2O along with Freons plays a crucial role in the destruction of stratospheric ozone and hence maximum effort is expended to decrease its discharge to the atmosphere. As mentioned above, high-temperature catalytic processes are most often used for the neutralisation of nitrogen oxides. However, electrochemical reduction of nitrous oxide has advantages over thermal destruction because the former process is not accompanied by the formation of by-products, *viz.*, NO_x. Reduction of N_2O to molecular nitrogen is thermodynamically favourable.

$$N_2O + 2H^+ + 2e^- \longrightarrow N_2 + H_2O,\ E^\circ = +1.77\ V.$$

The kinetics of electrochemical reduction on platinum electrodes in alkaline [272] and acidic [273,274] solutions was examined by cyclic voltammetry. A model was proposed [273,274] according to which adsorbed hydrogen plays the key role in reduction of N_2O.

$$N_2O\ (ads) + H\ (ads) \longrightarrow N_2\ (g) + OH\ (ads).$$

On the other hand, Ahmadi *et al.*[275] believed that decomposition of adsorbed nitrous oxide is the limiting stage of this process.

$$Pt-N_2O\ (ads) \longrightarrow N_2\ (g) + Pt-O.$$

The stage of subsequent reduction on the electrode, on the contrary, proceeds very rapidly.

$$Pt-O + 2H^+ + 2e^- \longrightarrow Pt + H_2O.$$

Electrochemical reduction of N_2O on other metal [276,277] and semiconducting oxide [278,279] electrodes was investigated. With Au, Pd, Cu, Ag, ZnO or In_2O_3, high current efficiency was achieved.

Tetraaza[14]annulene-nickel complexes,[269,280] cobalt porphyrins,[281,282] myoglobin [283] and iron–molybdenum complexes [284] fixed on graphite electrodes can be used as catalysts of electrochemical reduction of nitrous oxide.

A possibility of performing the destruction of NO_x on a cathode under conditions of a gas diffusion electrode seems to be promising. Both platinum [285] (or modified platinum [286,287]) electrodes and electrodes prepared from other transition metals [288] are employed as cathodes. In all cases, reduction of N_2O to N_2

proceeds smoothly without the formation of by-products. In addition, it was demonstrated [285] that N_2O-H_2 (1 M KOH) fuel cells can be used as chemical sources of electrical current.

Catalytic reduction of N_2O with atomic hydrogen was successfully carried out in a special electrochemical membrane-type reactor.[289] Reduction of nitrous oxide with carbon monoxide was also performed in an electrolytic cell supplied with a solid oxide electrolyte.[290]

Considerable attention is given to the development of electrochemical methods for the analysis of nitrous oxide in liquids.[291, 292] These methods, unlike chromatographic methods, allow one to monitor changes in the N_2O content on-line. Undoubtedly, these gas analysers will find wide use in medicine, food industry and systems of environmental monitoring.

3. Radiation-induced reactions in aqueous media

Ionising radiation in water induces processes giving rise to radicals, ions and stable species:[293]

Product of water radiolysis	$^{\bullet}OH$	$^{\bullet}H$	e^-_{aq}	H_2	H_2O_2	H_3O^+
Radiochemical yield G /μmol J^{-1}	0.29	0.06	0.29	0.04	0.08	–

In aqueous solutions saturated with N_2O, solvated electrons e^-_{aq} react with nitrous oxide to give the $^{\bullet}OH$ radicals, the total radiochemical yield [$G(^{\bullet}OH)$] of the latter being increased to ~ 0.58 μmol J^{-1}.

$$N_2O + e^-_{aq} \longrightarrow {}^{\bullet}OH + N_2 + OH^-.$$

This procedure for the generation of hydroxyl radicals, which are powerful electrophilic oxidants, is rather widely used in the laboratory practice.[294, 295] In addition, the ability of N_2O to react with solvated electrons attracts attention of researchers engaged in the application of ionising radiation to purification of sewage. It is well known that radiation treatment (cathode-ray or gamma radiation) in combination with other chemical or biological methods for the purification of liquid waste often proves to be convenient for the decomposition of harmful impurities.[296] The efficiency of this purification can be improved by introducing compounds which transform water radiolysis products to radicals acting as reductants (oxidants).[297, 298] Bubbling of nitrous oxide through sewage may improve the efficiency of the purification process.[299] However, the presence of N_2O sometimes substantially impairs the efficiency of this process.[298]

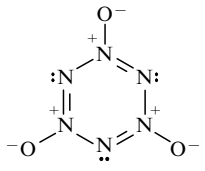
Not only gamma radiators or cathode-ray accelerators, but also ultrasonic probes and UV lamps can be employed as sources of ionising radiation. Thus photoinduced oxidation of aqueous solutions of Am(III),[300] Np(IV), Pu(IV),[301] aliphatic alcohols [302] and amino acids [303] saturated with nitrous oxide was reported. Shilov *et al.*[304] demonstrated that $\sim 35\%$ of Np(V) existing as a suspension of its hydroxide in 1 M LiOH solution saturated with N_2O was converted into Np(VII) upon sonication (44 KHz) for 40 min.

Oxidation of organic substrates with nitrous oxide under the action of ionising radiation can occur both in the gas phase [305] and in non-aqueous media.[306]

4. Nitrous oxide oligomers as potential high-energy materials

Semiempirical calculation procedures are finding increasing application in the search for new high-energy fuels and explosives. Before proceeding to the development of procedures for the synthesis of this type of compound, calculations are performed to elucidate whether conditions necessary for the preparation of the desired high-energy compound are fulfilled.

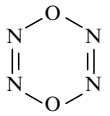
In a series of studies, calculations for hypothetical nitrous oxide oligomers were performed. Thus, Vol'pin *et al.*[307] examined the possibility of the existence of the cyclic trimer $(N_2O)_3$ (**18**). The heats of its formation (ΔH_0) calculated by different methods are given in Table 7.



18

The potential barrier to the $(N_2O)_3 \rightarrow 3\,N_2O$ decomposition reaction of the benzene-like molecule **18** (the ΔE_a value varies from 33 to 85 kcal mol^{-1}) is rather high, and it could exist due to kinetic stability.

Selected geometric and thermodynamical parameters (see Table 7) of the hypothetical cyclic structure N_4O_2 (**19**) were discussed.[308, 309]



19

Jones [308] believed that the N_4O_2 molecule is planar (the symmetry group D_{2h}). However, Manaa and Chabalowski [309] reasoned that this conformation is only intermediate one between two equivalent boat conformations (the symmetry C_{2v}). According to the calculations performed by these authors, the potential barrier to this transformation is approximately 7–10 kcal mol^{-1}.

Table 7. Heat of formation ΔH_0 of nitrous oxide cyclic oligomers.

Oligomer	ΔH_0 /kcal mol^{-1}						Ref.
	MINDO/3	MNDO	AM1	DZPSCF	MP_2	QCSISD	
18	−17	−48	−155				307
19	−48.5	−3.2	−82.0				308
				−86.3	−100.5	−78.5	309

The assumed structures and properties of open-chain,[310] crown-like [311] and $(NO)_3$-grafted [312] nitrous oxide oligomers were considered with the use of *ab initio* calculations. Jones and Csizmadia [310–312] believed that the occurrence of such metastable compounds is quite possible. The authors reasoned that high pressures, which have become accessible in recent years, can provide a decrease in the activation energy necessary for polymerisation of nitrous oxide and favour the formation of these unusual structures.

It should be noted that the $(N_2O)_n$ polymers in the form of ionic clusters [313, 314] or weakly bound complexes [315, 316] have long been known. However, these systems are of no interest as high-energy compounds. Thus the trimer of nitrous oxide, which has been observed in a molecular beam by IR spectroscopy,[315] exists as a non-planar acyclic weakly bound molecular complex characterised by the energy of dissociation into monomers equal to ~ 3.5 kcal mol^{-1}.

5. Nitrous oxide in the supercritical state

In the late 1980's, liquids in the supercritical state rekindled interest owing to their unique properties and unusual sensitivity with respect to small changes in the state parameters. The major fields of their application are supercritical liquid extraction,[317] chromatography [318] and synthetic chemistry.[319, 320]

Nitrous oxide in the supercritical state [N_2O(sc)] is more polar than CO_2(sc), which allows one to use the former with greater success both for extraction of different organic compounds [321, 322] and as a mobile phase in chromatography.[323, 324] In the synthetic chemistry, N_2O(sc) can be employed either as a reagent [195] or as a solvent.[325] Oxidation of tertiary phosphines with N_2O(sc) or with

the $N_2O(sc)/CO_2(sc)$ mixture was performed.[195] However, attempts to oxidise other classes of organic compounds, including compounds sensitive to oxidation by atmospheric oxygen, such as aldehydes, failed.[195] Poh *et al*.[195] reported that secondary alcohols can be oxidised under analogous conditions in the presence of palladium black. In addition, in some cases[326, 327] the use of $N_2O(sc)$ in the presence of rather low concentrations of organic compounds led to explosions. This is a serious obstacle to the wide application of $N_2O(sc)$ as a reagent. However, it is believed that the use of co-solvents, two-phase systems or carefully selected conditions can make these reactions less dangerous.

VII. Conclusion

Analysis of the data published over the last fifteen years demonstrated that the majority of studies concerned in one way or another with nitrous oxide have been carried out within the framework of either the environmental chemistry or heterogeneous catalysis. It should be noted that these lines of investigation are closely related.

On the one hand, there is a need to diminish the emission of nitrous oxide by 70% – 80% to stop an increase of its content in the atmosphere. This aim should be aided by employing new selective catalysts of decomposition of nitrous oxide in motor vehicles, heating and power plants and industrial processes. On the other hand, there are grounds to believe that N_2O will be used as one of the major oxidants in industry. Presently, procedures for the preparation of nitrous oxide by direct oxidation of ammonia over a catalyst are being developed.[167, 328, 329]

In our opinion, in the coming years the major efforts will go into the solution of problems associated with catalytic activation (destruction) of N_2O and ecological monitoring of nitrous oxide in the atmosphere.

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