STRUCTURE AND REACTIVITY OF THE NITROGEN DIOXIDE-DINITROGEN TETROXIDE SYSTEM

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NITROGEN dioxide was first prepared in 1777 by Priestley [1] by two different methods : the action of heat on lead nitrate and the action of concentrated nitric acid on copper. On the small scale lead nitrate is still useful as a source of nitrogen dioxide,[2] but the gas is made in large amounts today during the manufacture of nitric acid by the oxidation of nitric oxide.

The association $2NO_2 \rightleftharpoons N_2O_4$ is among the classic cases of mobile equilibrium. The shifting equilibrium is mirrored in the changing physical properties such as colour, density, and magnetism, and measurements of these quantities have been used to determine the equilibrium constant of dissociation and this in turn to interpret other behaviour, such as the dependence of its thermal conductivity on temperature. Equilibrium is established very rapidly, and only in recent years have reliable measurements of the rate at which equilibrium is attained been made.

The nitrogen dioxide equilibrium mixture is extremely reactive, entering into chemical changes as diverse as corrosion and esterification. In interpreting a particular reaction the first problem is to determine whether NO_2 or N_2O_4 is the reacting species. Reliable equilibrium data are the basis of this decision and the distinction is not usually difficult. Thus in gas-phase reactions at high temperature, nitrogen dioxide monomer greatly outweighs the dimer, while in the pure liquid the reverse is true. However, even when reaction has been assigned to the appropriate species an extraordinary diversity of behaviour remains to be explained ; in this Review attention is focused on the principles which permit the complexities to be analysed. When this is done all the diversity of chemical behaviour may be accounted for by a relatively small number of types of individual reaction steps combined in many different ways. This approach also permits closer attention to be given to the probable configuration of the transition state in reactions.

Because of current interest in the systems a brief discussion of flames supported by nitrogen dioxide is included : work on the role of the dioxide as a sensitising agent for reactions such as the oxidation of hydrogen and hydrocarbons has contributed less to its chemistry than to the systems it sensitises and is not considered here.

Structurally, the nitrogen dioxide system offers a number of problems.

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[1] Priestley, see Meldrum, *J.*, 1933, 905.

[2] Dodd and Robinson, " Experimental Inorganic Chemistry ", Elsevier, Amsterdam, 1954, 234.

The monomer NO_2 is the only known stable triatomic molecule with 17 valency electrons. The series, NO_2^+, NO_2, and NO_2^-, though paralleled by ClO_2^+, ClO_2 and ClO_2^-, is at present the only one to have been examined structurally—it will be even more noteworthy when the structure of the nitroxylate ion, NO_2^{2-}, is determined. Combined nitrogen dioxide is found as nitro-derivatives, X–NO_2, and nitrites, Y–ONO : structurally, dinitrogen tetroxide is a particular example of combined nitrogen dioxide ; although the structure has yet to be determined unequivocally the available evidence favours the form $O_2N–NO_2$.

Systems analogous to nitrogen dioxide–dinitrogen tetroxide are known. The dinitrogen tetroxide solvent system is closely related to the nitrosyl chloride system and formally resembles that of sulphur dioxide. Sometimes the analogies are extensive and reach beyond a few common reactions. The chlorine oxides promise to show related behaviour, both as monomers and dimers, and the work which has already been done on the nitrogen dioxide system will form a valuable basis for comparison.

Physical Properties

The Equilibrium Mixture.—Work before 1935 may be found in Gmelin's text ;[3] among recent work that of Giauque and Kemp [4] on thermodynamic properties is outstanding. Also noteworthy is that of Sage and his associates on the equation of state [5] and of Addison and his associates [6] on electrical properties. Only the salient features are summarised here.

At low temperatures nitrogen dioxide is a colourless solid whose density is about 1·95 g.cm.$^{-3}$. The lattice is body-centred cubic with six N_2O_4 molecules in the unit cell (side 7·77 ± 0·1 Å).[7] The heat capacity increases monotonically up to the triple-point, $-$ 11·2° C (261·90° K).

The liquid can be strongly supercooled (vapour-pressure measurements have been made at $-110°$) ; at the triple-point it is yellow. The vapour pressure is 13·978 int. cm. Hg. The liquid darkens as the temperature is raised. Under atmospheric pressure the liquid boils at 21·15°;[4] the critical constants [5] are $T_c = 158·2°$, $P_c = 100·0$ atm., $V_c = 165·3$ cm.^{3} (mole N_2O_4)$^{-1}$.

Liquid dinitrogen tetroxide (d, 1·49 g. cm.$^{-3}$ at 0°) has an extremely low electrical conductance (specific conductivity, $\varkappa \sim 10^{-12}$ mho) and a low dielectric constant ($\sim$2·42).[8]

Solubilities in dinitrogen tetroxide are said to follow those in diethyl ether.[9] It is not an ionising solvent : no simple salts are soluble in it and carboxylic acids are associated. Complete freezing-point data for its

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[3] Gmelin, " Handbuch der anorganische Chemie ", Deutschen Chemischen Gesellschaft, 8th edn., Vol. 4 (p. 782 *et seq.*), Berlin, 1936.

[4] Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.

[5] Reamer and Sage, *Ind. Eng. Chem.*, 1952, **44**, 185.

[6] Addison, Allen, Bolton, and Lewis, *J.*, 1951, 1289.

[7] Broadley and Robertson, *Nature*, 1949, **164**, 915.

[8] Addison, Bolton, and Lewis, *J.*, 1951, 1294.

[9] Frankland and Farmer, *J.*, 1901, **79**, 1356.

mixtures with nitrosyl chloride (NOCl),[10] dinitrogen trioxide[11] and pentoxide,[12] and sulphur trioxide[13] are available. Many organic compounds dissolve without reaction, *e.g.*, saturated hydrocarbons, aromatic hydrocarbons, halogeno- and nitro-compounds, and carboxylic acids. Substances which react with it include unsaturated hydrocarbons, alcohols, amines, and ketones. Phase diagrams of the following organic compounds which form simple eutectic mixtures with dinitrogen tetroxide have been plotted;[14, 15] nitromethane, trichloronitromethane, methyl iodide, bromoform, chloroform, carbon tetrachloride, bromobenzene, trinitrotoluene, and picric acid. Ethers, tertiary amines, and oxygen- and nitrogen-containing heterocyclic compounds form compounds.[16]

It is in gaseous nitrogen dioxide that the shifting equilibrium shows itself. At the normal boiling point the vapour contains 16·1% of NO_2 monomer and is brown. As the temperature is increased the proportion of monomer increases; by 150° the vapour is black. This change in colour and the accompanying change in vapour density are the best-known manifestations of the changing proportions. Other consequences are that the expansion coefficient, specific heat, and thermal conductivity all pass through maxima[3] at temperatures ranging from 40° to 65°. The equation-of-state data[17] are now available over a wide range of conditions extending up to 165° and pressures of 400 atm.

The Equilibrium $N_2O_4 \rightleftharpoons 2NO_2$.—This association was one of the first reversible reactions to be investigated quantitatively and to be interpreted in terms of the law of mass action. Numerous experimental methods have been used to determine the composition of the equilibrium mixture in the gaseous, liquid, and solid states. Measurements have been made recently to determine the rate at which equilibrium is attained in the gas phase.

Equilibrium in the gas phase. The degree of dissociation, α, at any temperature (° K) can be obtained from simultaneous measurements of pressure, P, and either density, D, or volume, V (litres):

$$\begin{array}{ccc} N_2O_4 & \rightleftharpoons & 2NO_2 \\ (1-\alpha)n & & (2\alpha)n \\ (PV)_{\text{obs.}} & = & (1+\alpha)nRT \end{array}$$

where n is the total number of moles present expressed as N_2O_4. These formulæ apply to ideal gases. Small deviations from ideality may be allowed for by equations of the type:

$$PV = RT(1 + \lambda P)$$

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[10] Addison and Thompson, *J.*, 1949, 218.

[11] Whittaker, Sprague, Skolniks, and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 4794.

[12] Lowry and Lemon, *J.*, 1936, 6.

[13] Seel and Meier, *Z. anorg. Chem.*, 1953, **274**, 197.

[14] Pascal, *Bull. Soc. chim. France*, 1923, 539.

[15] Addison, Hodge, and Lewis, *J.*, 1953, 1338.

[16] Addison and Lewis, *Quart. Rev.*, 1955, **9**, 115.

[17] Schingler and Sage, *Ind. Eng. Chem.*, 1950, **42**, 2158.

Three outstanding sets of measurements have been made[18–20] and correlated,[4] the results being best expressed in terms of the equilibrium constant :

$$K_p = \alpha^2 P/(1 - \alpha)$$

As a useful approximation at 25° (298·2° K) :

$$K_p \text{ (atm.)} = 0{\cdot}1426 - 0{\cdot}7588n/V$$

Precise data over a range of temperatures are given by Giauque and Kemp.[4] Graphical representations, *e.g.*, plots of values of K_p/P against T or of α against K_p/P, are given by Gmelin.[3]

Equilibrium in the condensed phase. In an *ideal* solution in which all the components obey Raoult's law :

$$(K_c^{\text{soln.}}/K_c^{\text{gas}}) = (RT/V_0)\,(P_{N_2O_4}/P_{NO_2}{}^2)$$

where the K_c's are equilibrium constants in moles per litre, V_0 is the volume per mole of solution and the P's are the (hypothetical) vapour pressures of the pure liquid species.[21] Thus, at a given temperature

(*a*) $K_c^{\text{soln.}} \neq K_c^{\text{gas}}$ (= 382 mole litre^{-1})

(*b*) The product K_cV_0 should be the same for all solvents

(*c*) $\Delta H_{\text{soln.}} - \Delta H_{\text{gas}} = L_{N_2O_4} - 2L_{NO_2}$

where L is the molar latent heat of the species shown in the subscript. For equilibrium in *real* solutions there are the data of Cundall[22] who used a colorimetric technique to measure α. Though the solutions are not ideal, and K_cV_0 is not constant, in all cases $K_c^{\text{soln.}}$ is less than K_c^{gas}. Thus, in carbon tetrachloride, $K_c \approx 8$, and in benzene, $K_c \approx 2$ (mole litre^{-1}).

The pure liquid appears to contain very little of the monomeric species ; Soné,[23] from measurements of paramagnetic susceptibility, estimates it at 0·7%. The pure solid is colourless and diamagnetic, and is assumed to contain only dinitrogen tetroxide.

Thermodynamic Functions for the Individual Species.—*Nitrogen dioxide.* Precise values are available for the entropies, $S°$, and free-energy functions $(G° - H_0°)/T$ for nitrogen dioxide from Giauque and Kemp's[4] treatment of accurate data for the $2NO + O_2 \rightleftharpoons 2NO_2$ equilibrium.[24] The results are in complete accord with the formulæ of statistical mechanics :

$$(G° - H_0°)/T = -257{\cdot}401 + \sum_{i=1}^{3} (G_{\text{vib.}}/T) - R \ln\,[gM^{3/2}T^4(I_1I_2I_3)^{\frac{1}{2}}/\sigma]$$

where $G_{\text{vib.}}$ is the contribution of each vibrational mode, g the electronic multiplicity, σ the symmetry factor, M the mass and the I's moments of

[18] Wourtzel, *Compt. rend.*, 1919, **169**, 1397.

[19] Bodenstein and Boes, *Z. phys. Chem.*, 1922, **100**, 75.

[20] Verhoek and Daniels, *J. Amer. Chem. Soc.*, 1931, **53**, 1250.

[21] See Moelwyn-Hughes, " Reactions in Solution ", 2nd ed., Oxford Univ. Press, 1947, p. 184.

[22] Cundall, *J.*, 1895, **67**, 794, 807.

[23] Soné, *Sci. Reports Tohôku Univ.*, 1922, **11**, (1), 148.

[24] Bodenstein and Katayama, *Z. Elektrochem.*, 1909, **15**, 244.

inertia of the molecule. The standard enthalpies and free energies of formation, however, still depend on the enthalpy of formation of nitric oxide which has not been precisely measured since 1880. The principal thermodynamic functions are listed in Table 1.

The ionisation potential of nitrogen dioxide has not been measured recently: discordant values are 11·0 ev from data on the appearance potential [25] and 12·3 ev from far-ultraviolet spectra.[26] The electron affinity of nitrogen dioxide has been derived from consistent (but empirical) values of the lattice energies of nitrites;[27] it is 1·62 ev.

TABLE 1. *Thermodynamic functions for gaseous nitrogen dioxide and dinitrogen tetroxide at* 298·16° K *and* 1 *atm.*

	NO_2	N_2O_4
$S°$ (calorimetric) . .	57·47	72·73 cal. deg.$^{-1}$ mole^{-1}
$S°$ (absolute) . . .	59·65	77·10 ,,
$\Delta S_f°$	− 14·46	− 71·12 ,,
$-(G° - H_0°)/T$ . .	49·202	59·106 ,,
$\Delta H_f°$	7964	2239 cal. mole^{-1}
$\Delta G_f°$	12,275	23,440 ,,
Ionisation potential .	250,000—283,000	— ,,
Electron affinity . .	37,300	— ,,

Dinitrogen tetroxide. The principal thermodynamic functions for dinitrogen tetroxide are also listed in Table 1. These were evaluated successfully by Giauque and Kemp [4] who used the third law of thermodynamics to correlate their calorimetric data with existing equilibrium measurements. Their method assumed for dinitrogen tetroxide a particular model in which there were no free internal rotations, but one classically excited vibration. The excellent consistency of their results completely upholds these assumptions. According to Wilson and Perkins [28] the weak vibration is the torsional oscillation ν_2 (Symmetry A_u) and, using Giauque and Kemp's [4] data, they derive for its frequency the value

$$\nu_4 = 4{\cdot}8 \times 10^{12} \text{ sec.}^{-1} \text{ (160 cm. }^{-1})$$

Reactions of Nitrogen Dioxide

Nitrogen dioxide is an odd-electron molecule and some of its reactions are typical of a free radical. Thus it acts as a radical when it associates with other radicals or atoms and when it dimerises, when it abstracts hydrogen from saturated hydrocarbons, and when it adds to unsaturated or aromatic compounds. In interpreting these changes comparison with well-investigated radicals such as methyl is most valuable. On the other

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[25] Smyth and Stueckelberg, *Phys. Rev.*, 1930, **36**, 472.
[26] Price and Simpson, *Trans. Faraday Soc.*, 1941, **37**, 106.
[27] Pritchard, *Chem. Rev.*, 1953, **52**, 555.
[28] Wilson and Perkins, unpublished results.

hand, reactions such as its photolysis, decomposition, oxidation, and reduction seem to owe little to its radical character.

The actual observed reactions of nitrogen dioxide are a complex pattern of its radical and non-radical modes of reaction. It is the shifting extents to which they, and their consequences, occur as the experimental conditions of temperature and pressure are altered that give rise to the observed complexity of, for example, its reactions with hydrocarbons. Three useful papers which analyse complex reactions and one review which collects much useful information may be quoted : the papers deal with the reaction with radicals,[29] with the nitration of hydrocarbons,[30] and with the reactions of the dinitrogen pentoxide system ;[31] the review [32] contains a collection (up to 1944) of the reactions with organic molecules.

This emphasis on the individual steps draws attention to the different possible types of activated complex. In general, two principal types exist : $X\cdots NO_2$ and $Y\cdots O{\cdot}NO$. This distinction is most readily made when nitrogen dioxide associates with a radical to form either a nitro-compound or a nitrite but it is apparent in all its reactions. The sections which follow are devoted to the different types of individual steps that occur : values of the velocity constants of different reactions are gathered together in Table 2.

The Association of Nitrogen Dioxide with Radicals.—When two radicals A· and B· collide they may either separate without forming a stable chemical bond or they may combine ; internal rotations and vibrations can serve as a temporary store for the energy of recombination until it can be passed on in collisions. Since combination is accompanied by a considerable decrease in enthalpy and entropy it is favoured by low temperatures. Further, the second-order velocity constant will depend on the pressure since the excess of energy must ultimately be removed by collisions with other species :

$$A\cdot + B\cdot + M \longrightarrow AB^* + M \longrightarrow AB + M^*$$

These associations have been observed often only in complex systems and detailed kinetic data are not available. In some cases, however, the reactions have been observed in reverse ($AB \longrightarrow A\cdot + B\cdot$) and afford indirect information about the association.

When nitrogen dioxide behaves as one of the radicals two distinct associations are possible.[29] Both nitro-compound and nitrite may be formed or may dissociate again :

$$X\cdot + NO_2 \rightleftharpoons X{\cdot}NO_2^* \longrightarrow X{\cdot}NO_2$$
$$X\cdot + NO_2 \rightleftharpoons X{\cdot}O{\cdot}NO^* \longrightarrow X{\cdot}O{\cdot}NO$$

When association yields a nitrite $X{\cdot}O{\cdot}NO$ and forms an X–O bond, the strength of the oxygen–nitrogen bond is frequently so low that the energy released on association is sufficient to break it almost immediately, yielding an XO· radical and nitric oxide :

$$X\cdot + NO_2 \longrightarrow XO{\cdot}NO^* \longrightarrow XO\cdot + NO$$

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[29] Gray, *Trans. Faraday Soc.*, in the press.

[30] Hass, Dorsky, and Hodge, *Ind. Eng. Chem.*, 1941, **33**, 1138.

[31] Johnston, *J. Amer. Chem. Soc.*, 1951, **73**, 4542.

[32] Riebsomer, *Chem. Rev.*, 1945, **36**, 157.

TABLE 2. *Kinetic data for reactions of nitrogen dioxide*

Class of reaction	Example	$\Delta H_{298}°$ (kcal.)	Kinetic order	Activation energy (kcal.)	Pre-exponential factor (l.-mole-sec. units)	Steric factor	Ref.
Radical–radical association	$2NO_2 \longrightarrow N_2O_4$	− 13	2	0	—	5×10^{-3}	33, 34
	$Cl + NO_2 \longrightarrow Cl{\cdot}NO_2$	− 29·5	2	—	—	—	39
	$NO + NO_2 \longrightarrow N_2O_3$	—	—	—	—	—	36
	$NO_3 + NO_2 \longrightarrow N_2O_5$	− 18 to − 22	—	1 ± 4	2×10^{10}	—	31, 35
Addition to unsaturated hydrocarbons	C_2H_4	—	3	12·5—18	$10^{8{\cdot}5}$—$10^{10{\cdot}9}$	—	53
	C_3H_6	—	3	13·6	$10^{9{\cdot}7}$	—	54
	C_2H_2	—	2	15	$10^{7{\cdot}1}$	—	55
Hydrogen abstraction	CH_4	—	2	21	10^6	—	41
	CH_2O	—	2	15·1—19	$10^{7{\cdot}1}$—10^9	—	45
	$CH_3{\cdot}CHO$	—	2	(16) 13·5	$(10^{9{\cdot}9})$ 10^7	—	46, 47
	$CHO{\cdot}CHO$	—	2	19·8	$10^{8{\cdot}9}$	—	45
Metathesis : Oxidation by NO_2	O	− 45	2	4	—	1	60, 61
	Na	∼ 0	2	2·4	—	—	62
	NO exchange	—	—	10·5	—	—	64
	NO_3 exchange	—	—	—	—	—	—
	O_2	—	2	50·2	$1{\cdot}2 \times 10^9$	10^{-2}	65
	CO	—	2	27·8	$4{\cdot}8 \times 10^8$	—	66
	SO_2	—	2	24·5	—	—	67
Metathesis : Reduction by NO_2	O_3	—	2	7 ± 0·6	$5{\cdot}9 \times 10^9$	—	70
	F_2	∼ 10	2	10·5	$1{\cdot}6 \times 10^9$	—	68
Metathesis : Decomposition	$2NO_2 \longrightarrow 2NO + O_2$	—	2	25	8×10^8	$\sim 10^{-2}$	72
	$NO_2 + NO_3 \longrightarrow NO_2 + NO + O_2$	—	—	5 ± 3	4×10^9	—	31

The net effect is thus the transfer of an oxygen atom ; such metatheses are discussed later (p. 372).

The best investigated association reaction is the association of nitrogen dioxide with itself to form dinitrogen tetroxide. As this reaction is too fast to be followed by conventional methods, shock waves have been used to provide a sudden change in the system $N_2O_4 \rightleftharpoons 2NO_2$ at equilibrium and the rate of reattainment of equilibrium then followed.[33, 34] It is found that the efficiency of recombination is 5×10^{-3}. If no activation energy is required for recombination this is the steric factor, P ; it is in the range expected for molecular association.

Another association for whose rate some data are available is the formation [35] of dinitrogen pentoxide by the combination of nitrogen dioxide and trioxide : for this the velocity constant, 4×10^9 l. mole^{-1} sec.$^{-1}$, has been interpreted in terms of a steric factor, P, of about 10^{-2} and activation energy, E, of 1 ± 4. Quantitative kinetic data are not available for the analogous reaction [36] with nitric oxide to form dinitrogen trioxide.

Association with alkyl radicals is the step responsible for the actual formation of nitroparaffins during the nitration of hydrocarbons. The factors affecting these reactions have been discussed by Gray.[29] In general all the associations lead to the formation of nitro-compounds and nitrites do not normally survive but are split at the O–N bond. This is due to the difficulty with which the excess of the energy of recombination is removed, especially in the gas phase. In solution, where deactivating collisions occur frequently, an example of a nitrite's being produced is known ; this is triphenylmethyl nitrite from the triphenylmethyl radical.

Other radicals whose association with nitrogen dioxide is recognised are hydroxyl, trichloromethyl, and perfluoroalkyl. Although only one of the two possible associations with the hydroxyl radical, that to form nitric acid, $HO{\cdot}NO_2$, has direct supporting evidence,[37] the other type of association, leading to pernitrous acid, $HO{\cdot}ONO$, has been investigated in reverse.[38]

When nitrogen dioxide associates with atoms a third body is necessary to remove the excess of energy, and third-order kinetics are observed in the association with atomic fluorine and chlorine.[39]

Hydrogen-abstraction Reactions.—The abstraction of hydrogen atoms from molecules is another characteristic reaction of free radicals which is shared by nitrogen dioxide :

$$RH + NO_2 \longrightarrow R{\cdot} + HO{\cdot}NO$$

This initial step is succeeded by rapid secondary reactions of the alkyl

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[33] Carrington and Davidson, *J. Phys. Chem.*, 1953, **57**, 418.
[34] Bauer and Gustavson, *Discuss. Faraday Soc.*, 1954, **17**, 69.
[35] Ogg, *J. Chem. Phys.*, 1953, **21**, 2079.
[36] D'Or and Tarte, *Bull. Soc. Sci. Liège*, 1951, **8–9–10**, 478.
[37] Johnston, Foering, and Thompson, *J. Phys. Chem.*, 1953, **57**, 390.
[38] Halfpenny and Robinson, *J.*, 1952, 928, 939.
[39] Cordes and Johnston, *J. Amer. Chem. Soc.*, 1954, **76**, 4264.

radical. Prominent among these are nitration by radical–radical association (p. 367) and oxidation :

$$R\cdot + NO_2 \longrightarrow R\cdot NO_2$$
$$R\cdot + NO_2 \longrightarrow RO\cdot + NO$$

Because of these competitive consecutive reactions overall reactions initiated by hydrogen abstraction are always complex ; their extent and path depend on temperature, pressure, the presence of catalysts, etc., and data are rarely complete. However the concept of the initial abstraction of a hydrogen atom can account satisfactorily for the rate and observed properties of a number of reactions. These include the reactions of nitrogen dioxide with alkanes [40]—methane,[41] propane,[42] the butanes, and higher homologues ;[30, 43, 44] and with the simple aldehydes—formaldehyde,[45] acetaldehyde,[46, 47] and glyoxal.[45] Values for the velocity constants are given in Table 2. Obviously such a step is easier the weaker is the original R–H bond. In accordance with this it is found that the ease of attack increases from hydrogen atoms attached to primary, through those attached to secondary, to those attached to tertiary carbon atoms in saturated hydrocarbons,[40] and is still easier in aldehydes where the bond, H–CRO, is even weaker. Thus in *iso*butane, $CHMe_3$, the " tertiary " C–H bond is specifically twelve times as reactive as the " primary " ; acetaldehyde is oxidised at 100—150° whereas propane, for example, reacts rapidly only at 350—450°. Exactly the same effect is found with oxygen. Conversely, olefinic and acetylenic carbon–hydrogen bonds are stronger than those in saturated paraffins and the addition of nitrogen dioxide takes precedence over abstraction of hydrogen.

In the nitration of paraffins in the vapour phase nitric acid is often used instead of nitrogen dioxide.[48] Nitric acid acts as a source of hydroxyl radicals and nitrogen dioxide ; the hydroxyl radicals initiate the reaction :

$$RH + \cdot OH \longrightarrow R\cdot + H_2O$$

while the nitroparaffin is actually produced by the radical R· associating with NO_2 as before. In the aldehydes the initial step is followed exclusively by oxidation since no corresponding stable nitro-compound exists :

$$R\cdot CHO + NO_2 \longrightarrow R\cdot CO\cdot + HO\cdot NO$$
$$R\cdot CO\cdot + NO_2 \longrightarrow R\cdot CO_2\cdot + NO \longrightarrow R\cdot + CO_2 + NO$$

Numerous other organic compounds, the ethers,[49] alcohols, ketones, fatty

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[40] Rout, *Trans. Faraday Soc.*, 1946, **42**, 281.

[41] Harnsberger, Thesis, University of California, 1951.

[42] Dorsky, Thesis, Purdue University, 1940.

[43] Urbanski and Slon, *Compt. rend.*, 1937, **204**, 870 ; for the general problem of nitration of aliphatic and aromatic compounds, see also a recent monograph by Urbanski, " Teoria Nitrowania ", Panstwowe Wydawnictwo Naukowe, Warsaw, 1955.

[44] Yoffe, *Research*, 1953, **6**, 75.

[45] Thomas, *Trans. Faraday Soc.*, 1953, **49**, 630.

[46] McDowell and Thomas, *Trans. Faraday Soc.*, 1950, **46**, 1037.

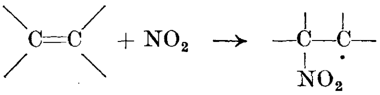
[47] Browning, personal communication.

[48] Bachmann, Hass, and Addison, *J. Org. Chem.*, 1952, **17**, 914.

[49] Hass and Hudgin, *J. Amer. Chem. Soc.*, 1954, **76**, 2692.

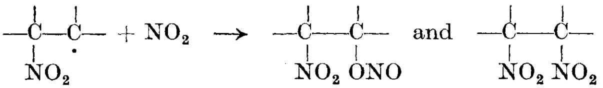
acids, and nitromethane,[41] have been made to react at high temperatures with nitrogen dioxide and products recorded although no kinetic data are available.

Addition of Nitrogen Dioxide to Unsaturated Compounds.—A large number of addition reactions is listed by Riebsomer (up to 1944).[32] Although very many different products have been isolated, the primary products of the addition to olefins are $\alpha\beta$-dinitro-compounds and α-nitro-β-nitrites, often in nearly equal proportions. Secondary reactions give rise to other species, and nitro-olefins, nitro-nitrates, and nitro-alcohols have all been found in solution while in the gas phase at high temperatures addition is followed by extensive oxidation. Similar reactions occur with halogenated olefins; for example, dinitro-compounds have been produced from perfluoroethylene.[52] Addition to unsaturated compounds has been interpreted in various ways; the older view was expressed in terms of complete or incipient heterolysis of dinitrogen tetroxide as $NO_2^+ \, NO_2^-$.[50] Evidence that addition occurs as $NO_2\cdot$ radicals rather than as $NO_2^+ NO_2^-$ or $NO^+NO_3^-$ comes from experiments with unsymmetrically substituted olefins.[51] It is found that addition of NO_2 at the terminal position occurs exclusively by the formation of a carbon–nitrogen bond: the second NO_2 group is added as either C–O·NO or C–NO_2. The same type of addition takes place irrespective of the electronegativity of the substituent groups:



$$>C{=}C< + NO_2 \rightarrow -\underset{NO_2}{\overset{|}{C}}-\overset{|}{\dot{C}}-$$

1(*a*)



$$-\underset{NO_2}{\overset{|}{C}}-\overset{|}{\dot{C}}- + NO_2 \rightarrow -\underset{NO_2}{\overset{|}{C}}-\underset{ONO}{\overset{|}{C}}- \text{ and } -\underset{NO_2}{\overset{|}{C}}-\underset{NO_2}{\overset{|}{C}}-$$

1(*b*)

Very few kinetic data are available, although ethylene and propene have been examined cursorily in the gas phase.[53, 54] The rate of reaction is approximately proportional to the olefin concentration and to the square of the concentration of nitrogen dioxide, but, despite this second power, the concentration of dinitrogen tetroxide produced is far too small at these temperatures (150—250°) for it to account for the observed rate of reaction. The kinetic data can be explained by reactions 1(*a*) being fast and 1(*b*) rate-controlling.[55] Otherwise the experiments are too slender for any detailed interpretation.

A free-radical addition mechanism has been advanced to explain the reaction with acetylenes. Thus, tolane (0—25°) forms both *cis*- and *trans*-dinitrostilbene,[56] but for an ionic mechanism the main product expected

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[50] Levy and Rose, *Quart. Rev.*, 1947, **1**, 358.

[51] Schechter and Conrad, *J. Amer. Chem. Soc.*, 1953, **75**, 5610.

[52] Haszeldine, *J.*, 1953, 2075.

[53] Cottrell and Graham, *J.*, 1953, 556.

[54] *Idem.*, *J.*, 1954, 3644.

[55] Thomas, *Trans. Faraday Soc.*, 1952, **48**, 1132.

[56] Campbell, Shavel, and Campbell, *J. Amer. Chem. Soc.*, 1953, **75**, 2400.

would be the *trans*-compound. Some kinetic data are also available for the reaction at 200° in the gas phase of nitrogen dioxide with acetylene, which is kinetically of the second order.[55]

Nitrogen dioxide also attacks aromatic hydrocarbons and it has been suggested that reaction is essentially the addition of one NO_2 molecule followed by the removal of a hydrogen atom by a second NO_2 molecule.[57] Further light on this reaction comes from nitration by pernitrous acid HO·ONO [38, 58] which both hydroxylates and nitrates. Reaction here is initiated by the addition of a hydroxyl group to form a radical which then associates with an NO_2 molecule. Subsequent elimination reactions explain the formation of all the observed products. The pernitrous acid experiments imply that in the presence of nitrogen dioxide alone two NO_2 molecules probably add on successively and that elimination of HO·NO follows. This has the same overall effect as Titov's mechanism.[57]

Metathetical Reactions.—When the association of nitrogen dioxide with alkyl radicals was discussed it was pointed out that the nitrite molecules R·O·NO formed could readily dissociate to form RO + NO. The transition state X····O····NO in the *oxidation* of any molecule by nitrogen dioxide must have much in common with a nitrite. On the other hand when nitrogen dioxide is itself oxidised by ozone for example, the transition state contains the nitro-group and not the nitrite group. The bimolecular *decomposition* of nitrogen dioxide itself belongs to a third class of metathetical reactions. Earlier (p. 367) the ambiguity arising out of the association of nitrogen dioxide with a radical X led to the formation of two distinct associated molecules, $X{\cdot}NO_2$ and X·ONO, having three possible types of re-dissociation leading to $(X\cdot + NO_2)$, (X· + ONO), and (XO· + NO); now there are at least three distinct associated molecules: ONO·ONO, $ONO{\cdot}NO_2$, and $O_2N{\cdot}NO_2$. An identical situation occurs in the reaction between nitrogen dioxide and trioxide.

Oxidation by nitrogen dioxide. Atoms of hydrogen,[59] oxygen,[60] nitrogen,[61] and sodium [62] are oxidised according to the equation

$$A + NO_2 \longrightarrow A\cdots O\cdots NO \longrightarrow AO + NO$$

and offer the simplest application of it. The reaction between oxygen atoms and nitrogen dioxide has been most studied; at room temperature 1 in 10^5 of the collisions which occur leads to reaction, the activation energy [60, 61] being about 4 kcal. mole^{-1}. For sodium atoms [62] it is about 2·4 kcal. mole^{-1}.

The oxidation of free radicals by nitrogen dioxide leads to the formation of alkoxy-radicals, RO, from alkyl radicals, and of acyloxy-radicals, RCO_2, from acyl radicals.[45, 46] These are themselves very reactive species and, in addition to undergoing, for example, association reactions they can also

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[57] Titov, *Zhur. obshchei Khim.*, 1948, **19**, 190.
[58] Heslop and Robinson, *J.*, 1954, 1271.
[59] Ashmore, *Research*, 1954, **7**, S35.
[60] Henriques, Duncan, and Noyes, *J. Chem. Phys.*, 1938, **6**, 518.
[61] Spealman and Rodebush, *J. Amer. Chem. Soc.*, 1935, **57**, 1474.
[62] Bawn and Evans, *Trans. Faraday Soc.*, 1937, **33**, 1571.

decompose. A normal alkoxy-radical, $R{\cdot}CH_2O$, decomposes by splitting off formaldehyde to leave a simpler alkyl radical. Exactly similar behaviour occurs with halogenated radicals. Thus the *n*-perfluoro-radicals are oxidised to perfluoroalkoxy-radicals ;[63] then carbonyl fluoride, *i.e.*, the fluorine analogue of formaldehyde, splits off leaving a simpler perfluoro-alkyl radical. These simpler radicals then repeat the same sequence.

Odd-electron molecules oxidised by nitrogen dioxide include nitric oxide, oxygen, and nitrogen dioxide itself. The exchange reaction between ^{15}NO and $^{14}NO_2$ occurs through an oxidation step *via* an intermediate compound $ON{\cdot}O{\cdot}NO$.[64] The reaction with oxygen to form nitric oxide and ozone is, of course, observed only as the rapid reverse reaction,[65] though sufficient thermodynamic data are available to derive the velocity constant of the forward reaction. Disproportionation of nitrogen dioxide to form nitric oxide and nitrogen trioxide is again observed [31] in reverse in the decomposition of dinitrogen pentoxide :

$$NO + NO_3 \longrightarrow 2NO_2$$

Carbon monoxide,[66] sulphur dioxide,[67] and nitrosyl chloride [68] are all oxidised by nitrogen dioxide. In mixtures of nitrogen dioxide with carbon monoxide (the latter in great excess to swamp the decomposition of the former) the reaction is of the first order with respect to each component, with $k = 4{\cdot}8 \times 10^8 \exp(-27{,}800/RT)$, but in mixtures also containing oxygen the reaction is faster than this and it has been suggested that nitrogen trioxide is an intermediate. The kinetics of the oxidation of sulphur dioxide have been investigated. Nitrosyl chloride is oxidised to nitryl chloride ; the kinetics of the reverse reaction are of the second order.[69]

Oxidation of nitrogen dioxide.

$$YO + NO_2 \longrightarrow Y{\cdots}O{\cdots}NO_2 \longrightarrow Y + NO_3$$

When nitrogen dioxide is oxidised the final product is dinitrogen pentoxide. The rate-determining step however is the transfer of an oxygen atom to the nitrogen dioxide molecule to form nitrogen trioxide ; the subsequent association of the dioxide and trioxide [35] (p. 369) is very fast.

Nitrogen dioxide is oxidised by ozone,[70] by nitryl chloride,[68] and by nitrogen trioxide.[71] The reaction with ozone has been investigated kinetically ; it is a fast reaction with a small activation energy and a steric factor of about 10^{-2}. The exchange reaction [31] between $^{15}N_2O_4$ and $^{14}N_2O_5$ involving the dissociations of dinitrogen tetroxide and pentoxide and the

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[63] Haszeldine and Francis, *J. Amer. Chem. Soc.*, in the press.

[64] Leifer, *J. Chem. Phys.*, 1940, **8**, 301.

[65] Johnston and Crosby, *ibid.*, 1954, **22**, 689.

[66] Crist and Brown, *ibid.*, 1941, **9**, 840 ; Crist and Calhoun, *ibid.*, 1937, **5**, 301.

[67] Kuz'miniukh, Turkhan, and Archipova, *Z. anorg. Chem.*, 1936, **226**, 310 ; Ilaniov, *J. Phys. Chem. U.S.S.R.*, 1941, **15**, 113.

[68] Ogg and Wilson, *J. Chem. Phys.*, 1950, **18**, 900.

[69] Freiling, Johnston, and Ogg, *ibid.*, 1952, **20**, 327.

[70] Johnston and Yost, *ibid.*, 1949, **17**, 386.

[71] Ogg, *ibid.*, 1947, **15**, 613 ; Ogg, Richardson, and Wilson, *ibid.*, 1950, **18**, 573.

exchange of partners is a form of oxidation since it involves the transfer of an oxygen atom from nitrogen trioxide to the dioxide.

To the same class of reaction belong the reactions of nitrogen dioxide with fluorine and chlorine to yield the corresponding nitryl halides.[68] Both these reactions are of the first order with respect to nitrogen dioxide and halogen and their rate is controlled by the step :

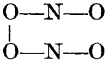
$$NO_2 + X_2 \longrightarrow XNO_2 + X$$

The decomposition of nitrogen dioxide. Although the decomposition of nitrogen dioxide involves loss of oxygen, it is a metathetical reaction which is not readily included in the previous sections on oxidation or reduction. It is a second-order reaction which has been well investigated kinetically ;[68, 71, 72] its activation energy is 25 kcal. and steric factor, P, about 10^{-2}. The reverse reaction between nitric oxide and oxygen has also been studied in detail and, by the principle of detailed balancing, whatever detailed mechanism is correct for it must, in reverse, be correct for the decomposition of nitrogen dioxide.

The simplest interpretation of the decomposition ascribes the formula $ON{\cdot}OO{\cdot}NO$ to the activated complex :

$$O{\cdot}NO + O{\cdot}NO \longrightarrow ON\cdots O\cdots O\cdots NO \longrightarrow ON + O_2 + NO$$

This satisfies both the simple triple-collision theory of the oxidation of nitric oxide and the more sophisticated transition theory of Gershinowitz and Eyring [73] who, in addition, specify the shape of the intermediate as (I).



$$\begin{array}{l} O{-}N{-}O \\ | \\ O{-}N{-}O \end{array}$$

(I)

It is also in agreement with Trautz's idea of successive bimolecular steps

$$O_2 + NO \longrightarrow NO_3 ; \quad NO_3 + NO \longrightarrow 2NO_2$$

if NO_3 represents the peroxynitrite radical $(O{\cdot}O{\cdot}N{\cdot}O)$ and not the nitrate radical $[O : N(O) : O]$.

Another reaction of this class is the elimination of oxygen from an $NO_2{\cdot}$ and an $NO_3{\cdot}$ radical. The same mechanism has been proposed :

$$ONO + ONO_2 \longrightarrow ON\cdots O\cdots O\cdots NO_2 \longrightarrow ON + O_2 + NO_2$$

The rate of this reaction derived from a study of the dinitrogen pentoxide system has been explained in terms of a steric factor of 10^{-2} and an activation energy of 5 ± 3 kcal. mole^{-1}.

To this class also belong the elimination of oxygen from two NO_3 radicals and of chlorine from nitryl chloride : this pair of reactions have the same formal relation to one another as the decomposition of nitrogen dioxide has to the decomposition of nitrosyl chloride.

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[72] Bodenstein and Ramstetter, *Z. phys. Chem.*, 1922, **100**, 106 ; Perrine and Johnston, *J. Chem. Phys.*, 1953, **21**, 2202.

[73] Gershinowitz and Eyring, *J. Amer. Chem. Soc.*, 1935, **57**, 985.

The Photolysis of Nitrogen Dioxide.[74]—The absorption of radiation and formation of excited NO_2 molecules is already marked at 6000 Å. The energy of excitation is not enough to dissociate the molecule and it is either quenched or re-radiated as fluorescence. The lifetime for the excited state (in the absence of collisions) is $4{\cdot}5 \times 10^{-5}$ sec. ;[75] fluorescent emission is continuous, extending up to 8000 Å. At shorter wavelengths absorption becomes diffuse and fluorescence fades as dissociation begins. At 4000 Å. the quantum yield, γ, is small. As the wavelength is decreased the quantum yield approaches 2.

$$NO_2 + h\nu \longrightarrow NO + O \quad ({}^3P \text{ or } {}^1D)$$
$$NO_2 + O \longrightarrow NO + O_2$$

A second diffuse region of the spectrum occurs near 2459 Å. These two distinct regions of absorption have been associated with the production of normal ^3P or excited ^1D oxygen atoms. A photostationary state is possible because of the recombination of NO and O_2 but at low pressures recombination is so slow that long irradiation is required to bring it about.

Flames Supported by Nitrogen Dioxide.—Interest in rocket fuels such as kerosene–nitric acid mixtures or nitrate esters has in recent years drawn attention to the importance of flame and combustion supported by nitrogen dioxide. Numerous investigations of spontaneous and spark ignitions have been made but outstandingly the most valuable modern work is that of Parker and Wolfhard [76] on stationary flames. General principles may be stated :

(i) Pyrolysis to nitric oxide and oxygen precedes oxidation.
(ii) With simple fuels such as hydrogen and carbon monoxide oxidation at one atmosphere's pressure does not proceed beyond the formation of nitric oxide. The flame has a single zone. No spectral bands characteristic of CN radicals are emitted.
(iii) With more complex fuels, *e.g.*, hydrocarbons, the flames show two distinct zones. In the first, decomposition as far as nitric oxide and oxidation by oxygen occurs ; only continuous radiation is emitted. In the second nitric oxide itself reacts ; CN, NH, and C_2 bands are emitted.

The following fuels have received attention : hydrogen,[59, 76] carbon monoxide,[77, 76] carbon disulphide,[78] the normal paraffins having 1—5 carbon atoms,[44, 76] ethylene,[76] acetylene,[76] formaldehyde,[79, 80] acetaldehyde,[80] methanol,[80] ethanol,[80] diethyl ether,[81] and methyl nitrite.[81]

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[74] Henri, *Nature*, 1930, **125**, 202 ; Norrish, *J.*, 1931, 1158, 1604, 1611 ; Baxter, *J. Amer. Chem. Soc.*, 1930, **52**, 3920 ; Holmes and Daniels, *ibid.*, 1934, **56**, 630.

[75] Neuberger and Duncan, *J. Chem. Phys.*, 1954, **22**, 1693.

[76] Parker and Wolfhard, Fourth Symposium on Combustion, Williams and Wilkins, Baltimore, 1953 ; Fifth Symposium on Combustion, Reinhold, New York, 1955.

[77] Buckler and Norrish, *Proc. Roy. Soc.*, 1939, *A*, **172**, 1.

[78] Berl and Barth, *Z. phys. Chem.*, *Bodenstein Festband*, 1931, 222.

[79] Pollard and Wyatt, *Trans. Faraday Soc.*, 1949, **45**, 767 ; 1950, **46**, 281.

[80] Gray and Yoffe, *J.*, 1950, 3180.

[81] Gray, Hall, and Wolfhard, *Proc. Roy. Soc.*, in the press.

Reactions of Dinitrogen Tetroxide

Pure liquid dinitrogen tetroxide contains more than 99% of the species N_2O_4, and its reactions might be expected to be those of this species. They may, of course, occur homogeneously or heterogeneously. In addition some examples of reactions of dinitrogen tetroxide in the homogeneous gas phase are known. Dinitrogen tetroxide is perhaps best known as the mixed anhydride of nitrous and nitric acids. This is only one aspect of the wider view of the dinitrogen tetroxide solvent system based on ionisation to NO^+ and NO_3^-. Ionisation is the first of its reactions to be considered; the tendency to form $NO^+NO_3^-$ is the basis of the interpretation of its chemistry. One of the most convenient laboratory preparations of dinitrogen tetroxide from nitrosylsulphuric acid ($NO{\cdot}SO_4H$) and potassium nitrate is the exact reverse of this reaction. Ionisation is encouraged by solvents of high dielectric constant, such as the strong acids phosphoric, sulphuric, and perchloric . it is also encouraged by the continuous removal of either NO_3^-, *e.g.*, as a complex ion by zinc nitrate, or of NO^+, *e.g.*, as a complex ion by a Lewis base. Similarly, solvents such as water, alcohol, and amines also remove NO^+ by reaction with it to form nitroso-compounds. Reducing agents such as electropositive metals and halide anions give up an electron to form the positive metal ion or the neutral halogen atom, and the NO^+ ends up as nitric oxide.

Ionisation : The Dinitrogen Tetroxide Solvent System.—Solubilities in dinitrogen tetroxide have been discussed earlier and it was stated that it is a very poor conductor of electricity. However, although stoicheiometrically ionisation is extremely small its existence * has been elegantly demonstrated by Clusius and Vecchi.[82] They dissolved tetramethylammonium nitrate, $(CH_3)_4{}^+N{\cdot}{}^{15}NO_3^-$, in dinitrogen tetroxide. Exchange of the nitrogen-15 isotope was found to be complete:

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

No evidence has been found for ionisation to NO_2^+ and NO_2^-. Ionisation is of course favoured by increased dielectric constant, ε. The pure liquid has $\varepsilon = 2{\cdot}4$ and $\kappa \sim 10^{-12}$ mho. In nitromethane $\varepsilon = 37$ and $\kappa \sim 10^{-6}$ mho. Despite this millionfold increase, ionisation is still minute stoicheiometrically. When a mixture of nitric acid and acetic acid is used as solvent, dinitrogen tetroxide behaves as a weak electrolyte. In pure nitric acid the conductivity resembles that of potassium nitrate; Raman spectroscopy shows that in solutions of dinitrogen tetroxide in nitric acid the greatest part is present as NO_3^- and NO^+ and there is very little N_2O_4 or NO_2.[83] (There is slight formation of NO_2^+ from the self-ionisation of the nitric acid.[84]) There is reason to believe that this NO^+ is not free but is solvated either by nitrogen dioxide, to form $N_2O_3^+$, or by dinitrogen tetroxide to form $N_2O_4{\cdot}NO^+$. In

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[82] Clusius and Vecchi, *Helv. Chim. Acta*, 1953, **36**, 930.

[83] Goulden and Millen, *J.*, 1950, 2620.

[84] Lynn, Mason, and Corcoran, *J. Phys. Chem.*, 1955, **59**, 238.

* There is a formal resemblance here to liquid sulphur dioxide, which has been said to behave as the source of SO^{2+} and SO_3^{2-} ions.

sulphuric acid ($\varepsilon \sim 110$) ionisation to NO^+ is complete.[85] Sulphuric acid is such a strong proton donor that when small amounts of dinitrogen tetroxide are dissolved in it, the nitric acid is converted quantitatively into NO_2^+:

$$N_2O_4 + H_2SO_4 = NO^+ + HNO_3 + HSO_4^-$$
$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$

but molecular HNO_3 is definitely present in a 20% solution of dinitrogen tetroxide.[86]

Nitrosyl-salt Formation.—As an extension of the previous section it may be mentioned that a number of nitrosyl salts, *e.g.*, $NO{\cdot}HSO_4$, $(NO)_2S_2O_7$, $NO{\cdot}H_2PO_4$, $NO{\cdot}ClO_4$, can be formed by dissolving dinitrogen tetroxide in strong acids.[87] Formation of these is, of course, accompanied by nitric acid and they are better prepared from dinitrogen trioxide.

Complex-salt Formation.—Zinc nitrate dissolves in dinitrogen tetroxide to form a compound $Zn(NO_3)_2,2N_2O_4$.[88] Its structure has been shown to be $(NO^+)_2[Zn(NO_3)_4{}^{2-}]$. The complex compound with uranyl nitrate, $UO_2(NO_3)_2,N_2O_4$, may be similarly formulated[89] as $NO^+[UO_2(NO_3)_3{}^-]$. Other salts also give rise to complexes which may be formulated in the same way. Formation of these compounds is a good example of ionisation of N_2O_4 to NO^+ and NO_3^- encouraged by continuous removal of NO_3^-.

Compound Formation.—A list of the compounds formed[16, 90-97] in liquid mixtures of dinitrogen tetroxide with a variety of substances such as amines, ethers, and nitriles is given in Table 3. The formulæ have been determined by the classical methods of cryoscopy, viscosity, and conductivity. The most frequent formula is $N_2O_4,2B$ (where B is the base) though N_2O_4,B is not uncommon. The equation for the dissociation equilibria applying to all the compounds is :

$$N_2O_4,2B \overset{a}{\rightleftharpoons} N_2O_4,B + B \overset{b}{\rightleftharpoons} N_2O_4 + 2B$$

The compounds are soluble in ether and in some halides, but not in hydrocarbons : there is some evidence from the shape of the freezing-point curves that the compounds exist in the liquid phase. The substances which form compounds are all typical Lewis bases such as tertiary amines, heterocyclic bases, ethers, and nitriles. All these molecules possess unshared electrons (lone pairs). The stability of the compounds, *i.e.*, the positions of the

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[85] Gillespie, Graham, Hughes, Ingold, and Peeling, *J.*, 1950, 2504.

[86] Millen, *J.*, 1950, 2600.

[87] See Moeller, " Inorganic Chemistry ", Wiley, New York, 1952.

[88] Addison and Lewis, *J.*, 1951, 2833.

[89] Addison and Hodge, *Nature*, 1953, **171,** 569.

[90] Addison, Hodge, and Sheldon, *Chem. and Ind.*, 1953, 1338.

[91] Addison, Conduit, and Thompson, *J.*, 1952, 1303, 1390.

[92] Rubin, Sisler, and Schechter, *J. Amer. Chem. Soc.*, 1952, **74,** 877.

[93] Ling and Sisler, *ibid.*, 1953, **75,** 5191.

[94] Whanger and Sisler, *ibid.*, p. 5158.

[95] Gibbins, Eichhorn, and Sisler, *ibid.*, 1954, **76,** 4668.

[96] Comyns, *Nature*, 1953, **172,** 491 ; *J.*, 1955, 1557.

[97] Davenport, Burkhardt, and Sisler, *J. Amer. Chem. Soc.*, 1953, **75,** 4175 ; Bachman and Feuer, Abs. of 128th Amer. Chem. Soc. Meeting, September 1955.

TABLE 3. *The dinitrogen tetroxide solvent system : formation of compounds with oxygen and nitrogen compounds*

Oxygen derivatives	No. of mols. of base in compound	Nitrogen derivatives	No. of mols. of base in compound	Nitriles, ketones, etc.	No. of mols. of base in compound
Diethyl ether	2	Trimethylamine	1, 2	Acetonitrile	1, 2
Di-*n*-propyl ether	2	Triethylamine	2	Benzonitrile	1
Di-*iso*propyl ether	2	Diethylnitrosamine *	2		
Di-*n*-butyl ether	2	*NN*-Dimethylaniline	1, 2	Acetone	2
Di-*tert*.-butyl ether	none	*NN*-Diethylaniline	2	Camphor †	4/5, 3/2
		N-Methyldiphenylamine	2		
Tetrahydrofuran	1, 2	*NN*-Dimethyl-*o*-, -*m*-, and -*p*-nitroaniline	none	Acetic acid	2
α-Methyltetrahydrofuran	2	*NN*-Dimethyl-*p*-nitrosoaniline	2		
Perfluorotetrahydrofuran	none	Pyridine	2	Acetic anhydride	1
Tetrahydropyran	2	α-Picoline	1, (2) ‡		
		β-Picoline	1, (2) ‡	Ethyl benzoate	2
1 : 2-Diethoxyethane	1	2 : 6-Lutidine	none		
		Quinoline	2		
1 : 4-Dioxan	1	2-Methylquinoline	none		
1 : 3-Dioxan	1	*iso*Quinoline	2		
Trioxan	1	Acridine	2		

* Diethylnitrosamine is included as its behaviour classes it as a tertiary amine.

† No explanation for the reported stoicheiometry of the camphor complexes has been offered though one of the compounds is near to 1 : 1, and experimental error may lead to these curious ratios.

‡ Incongruent m.p.

equilibria (*a*) and (*b*), depends on the nature of the solvent, the temperature (the compounds are stable only at low temperatures), and above all upon the base. The influence of the nature of the base is clearly shown by the investigation of nitrogen and oxygen bases which do not form addition compounds, *i.e.*, which give equilibria (*a*) and (*b*) both on the right-hand side. The three *NN*-dimethylnitroanilines [97] and perfluorotetrahydrofuran do not form compounds at all, presumably because of their electronegative substituents. The behaviour of the lutidines, 2-methylquinoline, and di-*tert.*-butyl ether can be explained by arguments involving steric hindrance. With the α- and β-picolines both compounds are formed but equilibrium (*a*) lies over to the right-hand side. The same is true of benzyl cyanide.

On the basis of measurements of electrical conductivity and absorption spectra the formulæ $B,NO^+NO_3^-$ [96] and $B_2NO^+NO_3^-$ have been ascribed to the nitrogen compounds.[90, 91] These are analogous to the base-stabilised halogen nitrates $(C_5H_5N)_2,Cl^+NO_3^-$ and $(C_5H_5N)_2,Br^+NO_3^-$. Similar formulæ satisfy the observed stoicheiometry in the ethers with one oxygen atom which give rise to compounds of the type $2B,N_2O_4$; compounds like dioxan give compounds B,N_2O_4. An alternative suggestion has been made by Sisler who reports that the spectra contain no line which might be expected from NO^+. However, even if ionisation were complete the $N{\equiv}O^+$ triple bond is not present in the base-stabilised cations which are $(B{-}N{=}O)^+$ and $(B_2{=}N{-}O)^+$ respectively. In fact in the media in which these compounds are formed ionisation is probably only incipient and the compounds are better described as base-stabilised nitrosyl nitrates $B,ON{\cdot}ONO_2$ and $2B,ON{\cdot}ONO_2$. As yet no *X*-ray data are available to decide the question.

This type of compound formation has been described as complementary to complex-salt formation in which ionisation is encouraged by removal of NO_3^- in the form of a complex anion (p. 377) : here it is the NO^+ which is removed. But even in the complexes the ions are present in pairs and an alternative description is that the compounds are base-stabilised nitrosyl nitrates. Further information about the structure of the complexes may be forthcoming from comparison with other charge-transfer complexes.

Reaction of Metals with Dinitrogen Tetroxide.—The reactions with dinitrogen tetroxide of many metals are listed in standard works on inorganic chemistry.[3] One clear generalisation emerges : all metals which react at low temperatures liberate nitric oxide and are converted into the appropriate nitrate :

$$M + N_2O_4 \longrightarrow MNO_3 + NO$$

This reaction may be described as the transfer of an electron from the metal to dinitrogen tetroxide which yields, not $NO^+NO_3^-$, but nitric oxide and nitrate ions. The equation represents the course of the low-temperature reaction with sodium,[98] potassium,[99] zinc,[99] silver,[99] and lead :[99] this is the reaction which occurs when nitrogen dioxide attacks the surface of mercury, in, for example a manometer. The most completely investigated metal is

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[98] Angus, Jones, and Phillips, *Nature*, 1949, **164**, 433.

[99] Addison and Thompson, *J.*, 1949, S211 ; Addison, Lewis, and Thompson, *J.*, 1951, 2829 ; Addison and Lewis, *ibid.*, p. 2833.

zinc. There is no evidence that the metal nitrite is ever formed directly, but reaction ends at that stage when the metal is strongly electropositive : amphoteric behaviour is shown by zinc nitrate which dissolves to form a complex anion. At high temperatures metals react to form a mixture of products, owing partly to attack by nitrogen dioxide and partly to decomposition of nitrates formed initially. Thus potassium burns with a red flame to form potassium nitrite as well as nitrate ; magnesium, manganese, iron, cobalt, and nickel form oxides.

Reaction of Dinitrogen Tetroxide with Anions.—Liquid and gaseous dinitrogen tetroxide react readily with many salts. In the majority of the reactions the cation is unaltered and it is the anion which is changed. These reactions may be generalised as the transfer of an electron from the anion, X^-, to dinitrogen tetroxide to yield the nitrate ion and nitric oxide :

$$N_2O_4 + X^- \rightarrow NO_3^- + NO + X \quad . \quad . \quad . \quad (2)$$

The discharged anion, X, may itself be a very reactive species and often undergoes further rapid and extensive changes. Examples of this are provided by the chlorides, bromides, iodides, and azides. Thus, moist potassium halides yield potassium nitrate but whereas with potassium chloride the nitric oxide is converted into nitrosyl chloride,[100] with potassium bromide free bromine is liberated.[3] The course of the reaction with iodides depends on the conditions :[101] solid potassium iodide or tetramethylammonium iodide reacts according to equation (2) where $X = \frac{1}{2}I_2$. In aqueous solution further changes are possible ; with metal azides [101] the nitrate is again formed but the hypothetical $N_3{\cdot}NO$ [102] (cf. Cl·NO) appears as nitrogen and nitrous oxide.

When reaction occurs between dinitrogen tetroxide and the solid MX, although the metal M may not appear to enter into reaction as written above, it exercises a strong influence on the free energy of the reaction through the dependence on M^+ of the lattice energies of MX and MNO_3.

When the anion is that of an oxy-acid, HOY, the general reaction can be described as the displacement of one acid anhydride (Y_2O) by another (N_2O_4) with the liberation of dinitrogen trioxide. This class of reaction includes those with the hydroxides of the alkali metals,[3, 103] for when dealing with the dinitrogen tetroxide system it is reasonable to compare the water which is displaced from a solid hydroxide with the acetic anhydride displaced from an acetate. Thus good yields of acid anhydrides have been obtained from sodium salts of, for example, acetic acid, propionic acid, butyric acid, succinic acid, and phthalic acid.[32] Dinitrogen tetroxide replaces carbon dioxide in carbonates with the simultaneous formation of nitric oxide.[103]

In aqueous solutions of the hydroxides the hydroxyl ions are replaced

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[100] Mehring, Ross, and Merz, *Ind. Eng. Chem.*, 1929, **21,** 379 ; Whittaker and Lundstrom, *J. Amer. Chem. Soc.*, 1934, **56,** 1323 ; Reed and Clark, *Ind. Eng. Chem.*, 1937, **29,** 333.

[101] Seel, Nogradi, and Breit, *Z. anorg. Chem.*, 1952, **269,** 102.

[102] Seel, Kisceri-Bocz, and Nogradi, *ibid.*, 1951, **264,** 298 ; Seel and Nogradi, *ibid.* p. 311.

[103] Addison and Lewis, *J.*, 1953, 1319.

by nitrite and nitrate anions as the reaction proceeds. However, the evidence is clear that nitrite ion is formed only as a secondary step. The primary reaction is with the water and not the hydroxide ion. It has recently been shown that dry sodium hydroxide yields 94% of nitrate and 2·5% of nitrite,[103] though it should be said that the formation of nitrite as a first step is not completely excluded, since nitrites are themselves oxidised by dinitrogen tetroxide both in aqueous solution and in the solid state. The same reaction occurs with oxides: calcium oxide and zinc oxide with liquid dinitrogen tetroxide yield only the nitrates. Of course, if either of these reactions is carried out at high temperatures both the decomposition of the nitrate and the reaction of dinitrogen tetroxide as NO_2 obscure the situation. A good example is the reaction between moist sodium chlorate and dinitrogen tetroxide which produces chlorine dioxide in good yield.[104] Once again either viewpoint is possible: although displacement of one mixed acid anhydride by another is a formal description of the complete process, electron transfer and the occurrence of intermediate reactions is probably a more useful one:

$$\begin{array}{ccl} N_2O_4 + ClO_3^- & \longrightarrow & NO_3^- + NO + ClO_3 \\ ClO_3 + NO & \longrightarrow & ON{\cdot}O{\cdot}ClO_2 \text{ (mixed anhydride)} \\ \text{(Odd-electron} & & \downarrow \\ \text{molecules)} & & \\ & & NO_2 + ClO_2 \end{array}$$

The same unifying principle of ionisation to $NO^+NO_3^-$ brings order into the reactions with other salts, the formation from dinitrogen tetroxide of the nitrate ion being made possible by the continuous reduction of NO^+ with electrons from an anion. The diverse behaviour is due to subsequent reactions of the radicals formed from the discharge of the different anions.

The Reaction of Dinitrogen Tetroxide with Hydroxylic and Amino-solvents.—In earlier sections attention was drawn to the tendency of dinitrogen tetroxide to ionise in solvents of high dielectric constant. In the solutions discussed the most extensive reaction was the formation of the appropriate nitrosonium salt, *e.g.*, $NO{\cdot}ClO_4$ from perchloric acid. Other solvents of high dielectric constant are water, the alcohols, ammonia, and the amines. In them ionisation leads quickly to nitrosation and the production of nitrous acid, an alkyl nitrite, or a nitrosamine: [16, 105]

$$(C_2H_5)_2NH + N_2O_4 \longrightarrow (C_2H_5)_2N{\cdot}NO + H^+ + NO_3^-$$

Some of these reactions have been studied in the homogeneous gas phase, and others heterogeneously. The reaction rate diminishes with temperature suggesting that N_2O_4 is the active species; this is confirmed by the actual rate equations. Thus the rate of absorption into water is proportional to the concentration of dinitrogen tetroxide;[106] the rate of reaction between

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[104] Novadel-Agene Corp., B.P. 663,239; *Chem. Abs.*, 1952, **46,** 5796; Tennants Consolidated Ltd., B.P. 663,218; *Chem. Abs.*, 1952, **46,** 5796.

[105] Hughes, Ingold, and Ridd, *Nature*, 1950, **166,** 642.

[106] Denbigh and Prince, *J.*, 1947, 790.

alcohols[107] or ammonia[108] and dinitrogen tetroxide is proportional to the first power of each reactant. The chemical equations are:

$$H_2O + N_2O_4 \longrightarrow HONO + H^+ + NO_3^- \qquad (3)$$

$$ROH + N_2O_4 \longrightarrow RONO + H^+ + NO_3^- \qquad (4)$$

$$R_2NH + N_2O_4 \longrightarrow R_2N{\cdot}NO + H^+ + NO_3^- \qquad (5)$$

In solution the proton is appropriately solvated. The equations describe the typical course of solvolysis of a mixed acid anhydride. Obviously the mechanism reflects again the tendency of dinitrogen tetroxide to act as $NO^+NO_3^-$, as proved in the nitrosation of alcohols. The truth of equation (4) was first shown by Yoffe and Gray;[109] later work by Samuel and Yoffe,[110] using ^{18}O-labelled alcohol, showed that nitrosation by NO^+ occurred.* In accordance with the existence of this ionic mechanism a polar surface is found to assist a reaction otherwise proceeding in the gas phase.[111]

Normally nitric acid always accompanies the nitroso-derivative. When nitric oxide is present, however, and dinitrogen trioxide exists in equilibrium with it, it reacts faster than does the tetroxide, and very few nitrate ions are found.[112, 113]

With ammonia and primary amines[3] reaction proceeds further and may be supposed to be, for example:

$$\begin{array}{rcl} NH_3 + N_2O_4 & \longrightarrow & \underset{\text{solvated } NO^+}{NO{\cdot}NH_3^+} + NO_3^- \\ NH_3 + NO{\cdot}NH_3^+ & \longrightarrow & \underset{\text{solvated } H^+}{NH_4^+} + NO{\cdot}NH_2 \longrightarrow N_2O + N_2 \\ \hline 2NH_3 + N_2O_4 & \longrightarrow & NH_4NO_3 + N_2 + H_2O \\ \hline \end{array}$$

Similarly

$$2R{\cdot}NH_2 + N_2O_4 \longrightarrow R{\cdot}NH_3{\cdot}NO_3 + N_2 + ROH \longrightarrow \text{nitrite}$$

It is instructive to consider the reaction with water more closely.† When dinitrogen tetroxide is dissolved in an excess of water, nitrous and nitric acids are formed in equal amounts:

$$N_2O_4 + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} HNO_2 + H^+ + NO_3^- . \qquad (6)$$

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[107] Fairlie, Carberry, and Treacy, *J. Amer. Chem. Soc.*, 1953, **75**, 3786.

[108] Falk and Pease, *ibid.*, 1954, **76**, 4746.

[109] Yoffe and Gray, *J.*, 1951, 1412.

[110] Samuel and Yoffe, *Bull. Res. Council Israel*, 1954, **4**, 88, 326; Anbar, Dostrovsky, Samuel, and Yoffe, *J.*, 1954, 3603.

[111] Kaemmerer, Collins, Raimondi, and Treacy, O.N.R. Report 392.

[112] Wayne and Yost, *J. Chem. Phys.*, 1950, **18**, 767.

[113] *Idem*, *ibid.*, 1951, **19**, 41.

* The reaction between dinitrogen tetroxide and $H_2{}^{18}O$ has been described by Anbar and Taube;[116] they found that under suitable conditions the tetroxide reacts as $NO^+NO_3^-$. † The complete phase diagram for the N_2O_4–H_2O system is complex.

Nitrous acid decomposes however into nitric acid, nitric oxide, and water, and the overall equation is represented by :

$$3N_2O_4 + 2H_2O \rightleftharpoons 2NO + 4H^+ + 4NO_3^- \qquad . \quad . \quad (7)$$

This equation may also be derived by considering nitrous acid to come into equilibrium rapidly with nitric oxide, nitrogen dioxide, and water; Abel [114] is responsible for this clarification. The rate at which equilibrium, according to Abel's equation (7), is approached is the difference between the rates of forward and reverse steps of reaction (4). Denbigh and his co-workers [106, 115] have applied Abel's assumptions to the problem of the reaction of dinitrogen tetroxide with water, as follows :

Beginning with the equation

$$-\,\mathrm{d}[N_2O_4]/\mathrm{d}t = \tfrac{3}{4}\{k_f[N_2O_4][H_2O] - k_r[H^+][NO_3^-][HNO_2]\}$$

they derive and confirm experimentally that :

$$-\,\mathrm{d}[N_2O_4]/\mathrm{d}t = k_a\{[N_2O_4] - C[N_2O_4]^{\frac{1}{4}}[NO]^{\frac{1}{2}}\}$$

The expressions written above have a simple interpretation in terms of the ionisation of dinitrogen tetroxide. Since

$$[H^+][HNO_2] = \mathrm{const.}[H_2NO_2^+] = \mathrm{const.}[H_2O][NO^+]$$

where $H_2NO_2^+$ is the nitrous acidium ion, *i.e.*, aquated NO^+, then :

$$-\,\mathrm{d}[N_2O_4]/\mathrm{d}t = \mathrm{const.}[N_2O_4][H_2O] - \mathrm{const.}[H_2NO_2^+][NO_3^-]$$

Set in this form, the rate of reaction of dinitrogen tetroxide with water is seen to be determined exactly by its net rate of ionisation.[116]

Structural Relations between Nitrogen Dioxide and its Derivatives and the Structure of Dinitrogen Tetroxide

Previous sections have dealt with the species NO_2 and N_2O_4 on an equal footing. In a discussion of structural aspects it is more satisfactory first to consider the place of free nitrogen dioxide in the series :

$$NO_2^+ \quad NO_2 \quad NO_2^- \quad NO_2^{2-}$$

and of combined nitrogen dioxide in the forms Y·ONO and $X{\cdot}NO_2$. Dinitrogen tetroxide, here considered in a separate section, is of course a particular example of combined nitrogen dioxide.

The Series NO_2^+, NO_2, NO_2^-, NO_2^{2-}.—The nitronium ion, NO_2^+, is well known both in solutions (*e.g.*, of dinitrogen pentoxide in sulphuric acid [117, 118]) and in solid salts.[87] Its best characterised reactions are nitration of aromatic compounds in acidic media to form nitro-compounds and esterification of alcohols to form nitrates. It has sixteen valency electrons and is thus isoelectronic with CO_2, N_3^-, BO_2^- and numerous other linear triatomic

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[114] Abel, *Z. phys. Chem.*, 1930, **148,** 337.

[115] Caudle and Denbigh, *Trans. Faraday Soc.*, 1953, **49,** 39.

[116] Anbar and Taube, *J. Amer. Chem. Soc.*, 1955, **77,** 2993.

[117] Cf. Ingold, " Structure and Mechanism in Organic Chemistry ", Bell, London, 1954.

[118] Gillespie and Millen, *Quart. Rev.*, 1948, **2,** 277.

groups. It too is linear and symmetrical.[119, 117, 120] Values [120] for the nitrogen–oxygen bond length lie between 1·06 and 1·15 Å (see Table 4).

TABLE 4. *Influence of number of valency electrons on shape, size, and force fields in the* NO_2 *series*

Species	NO_2^+	NO_2	NO_2^-	NO_2^{2-}
No. of valency electrons .	16	17	18	19
N–O bond length, Å . .	1·10	1·188	1·24	1·28
Interbond angle . . .	180°	134°	115°	110°
Vibration frequency, cm.$^{-1}$				
ν_1 (symm. str.) . . .	1400	1361	1325	1285
ν_2 (deform.)	537	770	831	885
ν_3 (asym. str.) . . .	2390	1668	1360	1200

Nitrogen dioxide is unique among triatomic molecules in having seventeen valency electrons; no isoelectronic species have been investigated. It is not linear. Electron-diffraction measurements [121] and more recently accurate infrared spectroscopy [122] have given the following dimensions of the molecule (electron diffraction results in parentheses): The apex angle is 134° 4′ ± 15′ (132° ± 3°) and the nitrogen–oxygen bond length 1·188 ± 0·004 Å (1·20 ± 0·2 Å). The collision diameter is 4·6 Å. Addition of the extra electron to NO_2^+ has thus led to a profound change of structure. The vibration frequencies [123] reflect a similar change: resistance to stretching is diminished while resistance to bending is increased.

The nitrite ion exists in alkaline solutions and in the solid state in a series of salts of alkali and alkaline-earth metals. Its reactions include that with a carbonium ion to yield mixtures of nitro-alkanes and alkyl nitrites [124] indicating that both the oxygen and the nitrogen atom are potential centres of electronic charge. With eighteen valency electrons it is isoelectronic with ozone and, like ozone (apex angle 116°), it is non-linear. This is proved by the appearance of its fundamental frequencies in both infrared [125] and Raman spectra.[126] Two recent *X*-ray measurements on sodium nitrite have yielded values for bond lengths as 1·233 [127] or 1·247 ± 0·035 Å [128] and angles as 115·7° or 114·2° ± 4°. The tendencies in bond-force

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[119] Teranishi and Decius, *J. Chem. Phys.*, 1953, **21,** 1116; Ingold and Millen, *J.*, 1950, 2612, 2606; Chédin, *Compt. rend.*, 1936, **202,** 220; 1936, **203,** 722; Cox, Jeffrey, and Truter, *Nature,* 1948, **162,** 259.

[120] Eriks and MacGillavry, *Acta Cryst.*, 1954, **7,** 430; Grison, Eriks, and de Vries, *ibid.*, 1950, **3,** 290.

[121] Claesson, Donohue, and Schomaker, *J. Chem. Phys.*, 1948, **16,** 207.

[122] Brown and Wilson, *ibid.*, 1954, **22,** 955; Moore, *J. Opt. Soc. Amer.*, 1953, **43,** 1045.

[123] Wilson and Badger, *Phys. Rev.*, 1949, **76,** 472.

[124] de la Mare, Hughes, Ingold, and Pocker, *J.*, 1954, 2930; see also Kornblum, Larson, Mooberry, Blackwood, Oliveto, and Graham, *Chem. and Ind.*, 1955, 443, for the preparation of nitro-compounds.

[125] Williams, *J. Amer. Chem. Soc.*, 1939, **61,** 2987.

[126] Newman, *J. Chem. Phys.*, 1952, **20,** 444.

[127] Carpenter, *Acta Cryst.*, 1952, **5,** 132.

[128] Truter, *ibid.*, 1954, **7,** 73.

constants noted earlier are reinforced. Resistance to bending is still greater in NO_2^- than in NO_2 and resistance to stretching is reduced.

Sodium nitroxylate is said [129] to be formed by the reaction between sodium nitrite and sodium in liquid ammonia as a brilliant yellow solid of formula Na_2NO_2. The nitroxylate ion, NO_2^{2-}, which has nineteen valency electrons is isoelectronic with the hypothetical molecule FO_2, with the ion F_2O^+, and, less directly, with the molecule ClO_2.

No other series similar to the present one has ever been reported; it represents a unique opportunity in valency theory, and sodium nitroxylate fully deserves further examination. Even in the three members already investigated the correlations are most striking. The simplest is the gradual closure of the apex angle as more electrons are fed in to the nuclear skeleton; the other alterations are no less marked.

The Derivatives of Nitrogen Dioxide: $X{\cdot}NO_2$ and $Y{\cdot}ONO$.—The members of the family just discussed were all symmetrical molecules with two identical chemical bonds. In the covalent nitrites, $Y{\cdot}ONO$, this symmetry is destroyed and single and double bonds are developed. There are, however, very few structural data. For nitrous acid 1·46 and 1·20 Å are reported for the length of single and double bonds with an oxygen–nitrogen interbond angle close to 120° in the *trans*-form.[130]

In the series $X{\cdot}NO_2$, however, where X is a univalent group, the same symmetry is retained. The electron distribution in such compounds may reasonably be expected always to lie between the extremes $X^+NO_2^-$ and $X^-NO_2^+$. Thus in these derivatives the ONO angle might be expected always to lie between 115° and 180°, as is found to be the case. Furthermore, on a simple view this angle can be expected to lie between 115° and 134° when X is less electronegative than NO_2, giving the molecule the character $X^+NO_2^-$, and between 134° and 180° when X is more electronegative than NO_2, giving the molecule character $X^-NO_2^+$. Although sufficiently accurate structural data are not available to reveal these differences of bond lengths and angles, identical arguments apply to the force fields and vibration frequencies, and this effect may be detected in their magnitudes.[131] Thus the asymmetrical stretching mode which occurs at 1360 $cm.^{-1}$ in the nitrite ion occurs at a frequency of 1550 $cm.^{-1}$ in nitroethane ($R^+NO_2^-$), at 1610 $cm.^{-1}$ in trichloronitromethane ($^+CCl_3NO_2^-$), at 1616 $cm.^{-1}$ in nitrogen dioxide, at 1625 $cm.^{-1}$ in trifluoronitromethane ($CF_3^-NO_2^+$) and at 2390 $cm.^{-1}$ in the ion NO_2^+.

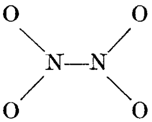
The Structure of Dinitrogen Tetroxide.—Potentially there are three separate problems, *viz.*, the solid, liquid, and gaseous state. In practice, no change in Raman spectrum occurs on melting and no difference has been found between the infrared spectrum of solid and gaseous dinitrogen tetroxide.[83, 132] Nor are there so many lines in the spectra as to suggest that more than one structure is present in appreciable amount. Four principal structures have to be considered.

[129] Zintl and Kohn, *Ber.*, 1928, **61**, 189; Maxted, *J.*, 1917, **111**, 1016.

[130] Tarte, *J. Chem. Phys.*, 1952, **20**, 1570.

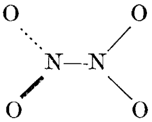
[131] Haszeldine, *J.*, 1953, 2525.

[132] Millen, personal communication.



(II)

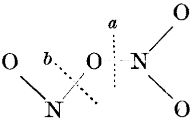
N–N link.
Planar.
Centre of symmetry.



(III)

N–N link.
Two NO_2 planes perpendicular.

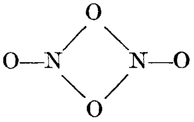
Interconvertible by free rotation.



(IV)

O–N link.

Two internal rotations.



(V)

Bridge formula.
Planar.
Centre of symmetry.

No internal rotations.

These formulæ all satisfy the ready dissociation of an N_2O_4 molecule into two NO_2 molecules [*e.g.*, in structure (IV) homolysis at *a*]. However, the very ease of their dissociation adds a further problem. Since there is always rapid production of nitrogen dioxide there are also pairs of NO_2 molecules in the act of collision, and these colliding pairs may have any of the formulæ (II), (III), (IV), (V) and while in this form may react. To interpret evidence for structure from chemical reactivity is thus very difficult and chemical must be given less weight than physical evidence. The existing items of physical evidence are as follows :

Calorimetry.[4] The low numerical value of the entropy favours a compact symmetrical formula (II), (III), or (V) rather than (IV) ; and the temperature dependence of the entropy almost completely excludes free rotation. The height of the barrier is about 10 kcal.[133] This also argues against formula (IV) which would be expected to possess two internal rotations. There is one classically excited vibration.

Spectroscopy. A lack of coincidences in infrared and Raman spectra [132] implies a centre of symmetry and excludes both formulæ (III) and (IV). On these data alone choice between structures (II) and (V) is not definite.

Dielectric-constant measurements.[134] Measurements of dielectric constant and refractive index indicate an unusually high electron- plus atom-polarisability, a property consistent with model (II) with a long nitrogen–nitrogen bond. This possibility obscures the interpretation of dielectric-constant measurements on gaseous mixtures of dinitrogen tetroxide and nitrogen dioxide.

X-*Ray measurements.*[7] Solid dinitrogen tetroxide has a cubic lattice. An assumed model (II) with N–N, 1·64 Å ; N=O, 1·17 Å ; and ONO angle, 126°, enabled possible *X*-ray reflections to be predicted and F-factors to be calculated. Experimental observation of the *X*-ray pattern from a single crystal gave 75% of the expected reflections and F-factors with average discrepancies of 16%.

Theoretical calculations. Model (II) has been used as the basis of theoretical calculations which lead to *r*(N–N) 1·57 Å ; *r*(N=O) 1·21 Å,

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[133] Bernstein and Burns, *Nature,* 1950, **166,** 1039.

[134] Addison and Lewis, *J.*, 1953, 1837 ; Williams, Schwingle, and Winning, *J. Amer. Chem. Soc.*, 1934, **56,** 1427 ; Schultz, *Z. Physik,* 1938, **109,** 517.

considered by the authors [135] to be satisfactorily close to the results of the studies with X-rays.

The planar structure (II) violates Pauling's empirical adjacent-charge rule,[136] and the combination of a long, weak nitrogen–nitrogen bond with strongly restricted rotation is not superficially attractive. However, the molecule B_2Cl_4 has recently been proved to be planar and not to show free rotation in the solid state although it has a long boron–boron distance.[137] If the bond which holds the two nitrogen dioxide moieties together is similar to the π-bond in ethylene this result may be explicable.

Prominent among the reactions of dinitrogen tetroxide is ready heterolysis [*i.e.*, fission at *b* in structure (IV)] to $NO^+NO_3^-$ which at first sight favours a formula of type (IV) or (V) rather than (II) or (III). However the oxalate ion, $C_2O_4^{2-}$, which has a structure of type (II) and is isoelectronic with N_2O_4 undergoes an identical change (see p. 389). Formula (II) is in accord with all the evidence presented and is the currently accepted model. It should be noted however that the bridge formula (V)[138] is not completely excluded by the existing data * and that it does give a very satisfactory explanation of both the strongly restricted rotation and the heterolysis to $NO^+NO_3^-$. A recent vibrational assignment on the basis of model (II) has been made.[140] Six of the frequencies (in cm.$^{-1}$) correspond to the three fundamentals of nitrogen dioxide, *viz.*, $\nu_1(A_g)$ 1334, $\nu_2(A_g)$ 811, $\nu_5(B_{1g})$ 1722; $\nu_{11}(B_{3u})$ 1240, $\nu_{12}(B_{3u})$ 748, $\nu_9(B_{2u})$ 1747. From the heat-capacity data $\nu_4(A_u)$ is 160. This torsional oscillation is spectroscopically inactive. On the basis of the doublet structure needed for a planar symmetrical structure, $\nu_{10}(B_{2u})$ is 430. By elimination $\nu_7(B_{1u})$, the only other infrared-active fundamental, is at 684 cm.$^{-1}$. The strongest Raman line, at 265 cm.$^{-1}$, is $\nu_3(A_g)$. It is then possible to assign the remaining Raman line at 500 cm.$^{-1}$ to $\nu_8(B_{2g})$. The 320 cm.$^{-1}$ frequency which can be derived from heat-capacity data is $\nu_6(B_{1g})$.

Work on the spectrum of the oxalate ion so far shows a close parallel to these figures, confirming the identity of the structure of N_2O_4 and of $C_2O_4^{2-}$.

Analogous Systems

Comparison of similar systems often draws attention to significant properties of each. It is interesting to compare the nitrogen dioxide–dinitrogen tetroxide system with (1) other nitrogen oxides, (2) other compounds of Group V elements, (3) the halogen oxides, and (4) with structurally analogous molecules.

The other odd-electron nitrogen oxides, nitric oxide and nitrogen trioxide,

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[135] Chalvet and Daudel, *J. Chim. phys.*, 1952, **49**, 77.

[136] Pauling, " The Nature of the Chemical Bond ", Cornell Univ. Press, 1945, p. 271.

[137] Atoji, Lipscomb, and Wheatley, *J. Chem. Phys.*, 1955, **23**, 1176.

[138] Longuet-Higgins, *Nature*, 1944, **153**, 408.

[139] Lippincott, unpublished work.

[140] Wilson, personal communication, 1955.

* It is preferred by Lippincott [139] on evidence from Raman spectra.

also undergo dimerisation and, in addition, they combine with nitrogen dioxide to form dinitrogen trioxide and pentoxide respectively. With one another they yield nitrogen dioxide ; this reaction, which demonstrates one aspect of the inter-relation of the oxides of nitrogen, is used in one of the standard laboratory preparations of dinitrogen tetroxide from the trioxide and pentoxide. The structure of the gaseous molecule $(NO)_2$ is not known ; even in the solid state it is not clearly defined. The structure of gaseous dinitrogen trioxide is disputed ($ON{\cdot}NO_2$ or $ON{\cdot}O{\cdot}NO$) ; although gaseous dinitrogen pentoxide is probably $O_2N{\cdot}O{\cdot}NO_2$ the solid is ionic, and gaseous dinitrogen hexoxide is probably $O_2N{\cdot}O{\cdot}O{\cdot}NO_2$.[141]

In the same way that dinitrogen tetroxide behaves as the basis of a solvent system $NO^+NO_3^-$ and is a mixed anhydride, so dinitrogen trioxide acts as $NO^+NO_2^-$ and dinitrogen pentoxide as $NO_2^+NO_3^-$ (both as pure anhydrides giving, *e.g.*, only one acid with water). On the same formal basis nitric oxide dimer is NO^+NO^-, the mixed anhydride of a hypothetical acid HNO and HNO_2, though, of course, it cannot be said to react in this way. On these grounds it could be suggested that nitric oxide would be the product of a reaction between K^+NO^- and $NO^+ClO_4^-$ just as the formation of N_2O_4 from NO^+ and NO_3^- is another of its standard methods of preparation.

Recently work has been done on the nitrosyl chloride solvent system based on NO^+Cl^-[142] and related to dinitrogen tetroxide in the same way as hydrogen chloride is to nitric acid. Nitrosyl chloride shares with dinitrogen tetroxide the properties of the nitrosonium ion ; *e.g.*, with alcohols it forms nitrites [143] and not hypochlorites. Like dinitrogen tetroxide also, when it reacts with olefins it appears to do so by attack as a free-radical rather than as an ionic form.

In Group V the ion SbO^+ belongs to the same family. Analogies among other members of the group again show diverse behaviour. Structurally, the dioxides, MO_2, of phosphorus, arsenic, and antimony have little in common with nitrogen dioxide. In the gas phase PO_2 exists as P_8O_{16}.[144] Solid antimonous oxide is supposed to consist of $Sb^{3+}Sb^VO_4^{3-}$ units.

In Group VII, however, closely similar situations do exist. The halogens, like the members of Group VA, form a diverse set of oxides. Among them chlorine dioxide, ClO_2, is another odd-electron molecule with many similarities to nitrogen dioxide. It gives rise to a series ClO_2^+, ClO_2, ClO_2^- and forms [146] a dimer, Cl_2O_4, which may behave as $ClO^+ ClO_3^-$. With water it reacts slowly yielding a mixture of chlorous and chloric acids :*

$$Cl_2O_4 + H_2O \longrightarrow HClO_2 + H^+ + ClO_3^-$$

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[141] Fichter and Brunner, *Helv. Chim. Acta*, 1929, **12**, 306.

[142] Burg and McKenzie, *J. Amer. Chem. Soc.*, 1952, **74**, 3143 ; Lewis and Wilkins, *Chem. and Ind.*, 1954, 634.

[143] Leermakers and Ramsperger, *J. Amer. Chem. Soc.*, 1932, **54**, 1837.

[144] Wells, " Structural Inorganic Chemistry ", 2nd edn., Oxford Univ. Press, 1950, p. 484.

[145] Halperin and Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 378.

[146] Brasted, " Comprehensive Inorganic Chemistry ", Vol. 3, " The Halogens ", Macmillan, London, 1954.

* The reaction between ClO_2 and $^{18}OH^-$ is described by Halperin and Taube.[145]

Iodine tetroxide, I_2O_4, shows the same behaviour [146] and acts as $IO^+IO_3^-$. The compounds $C_6H_5{\cdot}IO$ and $C_6H_5{\cdot}IO_2$ have been prepared and are similar to $C_6H_5{\cdot}NO$ and $C_6H_5{\cdot}NO_2$.

It has been argued by Lehmann and Krüger [147] that, since nitrogen belongs to Group V and chlorine to Group VII, in choosing similar systems for comparison a nitrogen oxide, NO_x, should be compared with a chlorine oxide, ClO_{x+1}. On this basis the equation

$$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

is replaced by

$$2ClO_3 \rightleftharpoons Cl_2O_6 \rightleftharpoons ClO_2^+ + ClO_4^-$$

This comparison is of a more formal nature than the previous one. Because of the relative unfamiliarity of the chemistry of the dimer of chlorine dioxide there is little doubt that existing work on dinitrogen tetroxide will be of value in interpreting and predicting reactions of the former.

Structurally, the guiding principle in the search for comparable compounds is the isoelectronic principle. This has been used in discussing the series NO_2^+, NO_2, NO_2^-, NO_2^{2-}. Parallels with NO_2^+ include substances as chemically diverse as carbon dioxide, beryllium fluoride (BeF_2) and the azide anion N_3^-: all of these possess the same linear structure. Nitrogen dioxide itself has the BF_2 radical and the ions O_3^+ and FNO^+ as suitable parallels : their structures are not yet known. Similarly ozone and nitrosyl fluoride are isoelectronic with the nitrite ion, NO_2^-. Like it they are not linear, but possess interbond angles all close to 115°. The nitroxylate ion NO_2^{2-} has the same number of electrons as the NF_2 radical and the (hypothetical) FO_2 molecule. Chlorine dioxide serves as a useful guide to suggest that the process of closing the angle from 180° reaches its maximum in this series with the nitroxylate anion.

Isoelectronic structural analogues of dinitrogen tetroxide are B_2F_4 and the oxalate * ion $C_2O_4^{2-}$. Diboron tetrafluoride is not known but the corresponding chloride has recently been shown to be planar and centrosymmetrical and to possess a long boron–boron bond.[137] This resemblance to dinitrogen tetroxide is most marked. Even more striking is the resemblance between the oxalate ion and dinitrogen tetroxide which extends beyond the structures and vibration frequencies to the chemical reactions of the two with concentrated sulphuric acid :

$$N_2O_4 \rightarrow NO^+ + NO_3^- \xrightarrow{2H^+} NO^+ + H_2NO_3^+ \xrightarrow{H^+} NO^+ + NO_2^+ + H_3O^+$$

$$C_2O_4^{2-} \rightarrow CO + CO_3^{2-} \xrightarrow{2H^+} CO + H_2CO_3 \xrightarrow{H^+} CO + CO_2 + H_3O^+$$

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[147] Lehmann and Krüger, *Z. anorg. Chem.*, 1953, **274**, 141.

[148] Dunitz, personal communication.

* The analogy between the oxalate ion and dinitrogen tetroxide serves as a reminder that, despite its chemical affinities, chlorine dioxide has structural differences from nitrogen dioxide. This will be demonstrated in Cl_2O_4 which is isoelectronic with P_2F_4 and $S_2O_4^{2-}$ and is almost certainly not a planar molecule : the dithionate ion, $S_2O_4^{2-}$, has been found to be non-planar.[148]

In the one system, heterolysis leads to oppositely charged ions : in the other to a neutral molecule and a doubly negative carbonate ion. Even the final products have similar structures, NO^+ and CO ; NO_2^+ and CO_2 being isoelectronic.

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