THE REACTIVITY AND STRUCTURE OF NITROGEN DIOXIDE

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I. INTRODUCTION

The red fumes of nitrogen dioxide were referred to in 1670 by W. Clark (89), who called the vapors by the alchemical name "the flying dragon." A century later (1777) the gas was prepared by Joseph Priestley (319), and in 1816 its empirical formula was established (296) independently by Dulong and Gay-Lussac. From these beginnings nitrogen dioxide has continued to grow in technical importance to the central position which it occupies today in the chemical industry of every major country.

This review is concerned with the structure, chemical reactivity, and physical properties of the nitrogen dioxide–dinitrogen tetroxide system. Structurally, the nitronium (NO_2^+) and nitrite (NO_2^-) ions are of considerable importance in these problems and their reactions are also considered in outline. As far as possible, only those reactions are discussed of which the mechanism is known, and the scope of the review has been deliberately limited to prevent duplication. Thus, a most valuable compendium (336) of reactions of nitrogen dioxide with organic molecules was published in 1945, enabling the authors to concentrate in this field on work done since then. Similarly, for references to work prior to 1935 on the inorganic reactions of nitrogen dioxide and the nitrites, Gmelin's *Handbuch* (156) is invaluable.

The chemistry of the NO_2–N_2O_4 system is very complex. In analyzing a particular reaction, the first problem is to determine whether NO_2 or N_2O_4 is the reacting species. Often, distinction is not difficult: thus, at high temperatures in the gas phase nitrogen dioxide is overwhelmingly the principal species present, whereas the pure liquid is almost pure dinitrogen tetroxide. The equilibrium data necessary to assist in making the distinction are available; these data are also essential in interpreting many of the physical properties of the equilibrium mixture. Even when reaction has been assigned either to nitrogen dioxide or to dinitrogen tetroxide an extraordinary diversity of behavior is found. In this review, attention is focussed on the principles which allow the initially bewildering complexity to be analyzed into its components. When this is done, a relatively small number of different types of individual reaction steps (e.g., atom transfer, addition) is found. It is the combination of these few different types of reaction in many different ways which leads to the diversity of chemical behavior observed.

When the experimental data are analyzed in this way, a number of valuable generalizations emerge. Dinitrogen tetroxide has for many years been recognized as the mixed anhydride of nitrous and nitric acids because of its reaction with water. From this review, the remarkably close parallel between water, alcohol, and ethers on the one hand and ammonia and the amines on the other both helps to place the water reaction in perspective and points the way to the still wider generalization—the formation of NO^+ and NO_3^- as separate entities or as ion-pairs. This ionization is the key not only to the behavior of the dinitrogen tetroxide solvent systems, but to nearly all the reactions assigned to dinitrogen tetroxide also. Thus, ionization is favored by solvents with a high dielectric constant, by the removal of either the NO_3^- anion or the NO^+ cation. The reactions may not stop here, and the many different secondary stages possible confer the extremely varied chemical properties found. Thus nitroso compounds are common products, and these include nitrous acid and the nitrites no less than nitrosoamines. Further possibilities exist in the presence of electron donors such as metals or anions, and the range of products is widened by the inclusion of these reactants. But again, ionization, incipient or actual, to NO^+ NO_3^- is the key to nearly every change.

Nitrogen dioxide is an odd-electron molecule and a number of its reactions are those of a free radical. Thus it both dimerizes and undergoes association reactions with other free radicals, adds to double bonds in unsaturated molecules, and takes part in hydrogen-abstraction reactions just as the methyl radical does. Other of its reactions, e.g., photolysis, decomposition, reduction, and oxidation, owe little to the free-radical properties but form other readily recognizable classes having much in common with one another. This classification enables inferences to be made about reactions only partially investigated; without it the chemistry of nitrogen dioxide would be a maze. The analytical approach may divert attention from the particular complex systems but compensates by showing clearly the path which further investigations should follow.

II. Preparation of Nitrogen Dioxide

Priestley, in 1777, was the first (296, 319) to carry out a laboratory preparation of nitrogen dioxide; he obtained it both by heating lead nitrate and by the action of strong nitric acid on copper. Numerous alternatives have been discovered since, but both of Priestley's original methods are convenient for small-scale preparation today. In the United States, but not in Europe, nitrogen dioxide is now marketed in cylinders.

A. FROM CONCENTRATED NITRIC ACID AND COPPER

When metals are dissolved in nitric acid, oxides of nitrogen are usually evolved; their relative abundance depends on the concentration of the acid and the temperature as well as on the metal. Concentrated (65 per cent and over) nitric acid at room temperature acts on copper, forming nitrogen dioxide, though later stages of reaction give rise to nitric oxide and nitrous oxide.

B. FROM LEAD NITRATE

Heavy metal nitrates are decomposed by heat, evolving oxygen and nitrogen dioxide, and leaving the oxide. Lead nitrate, which may readily be freed from moisture, is a convenient source of pure nitrogen dioxide.

$$Pb(NO_3)_2 \rightarrow PbO + \tfrac{1}{2}O_2 + 2NO_2$$

The lead nitrate is purified by recrystallization and dried at 110–120°C. Decomposition is conveniently carried out in a Pyrex tube heated electrically. A stream of dry oxygen carries the nitrogen dioxide over phosphorus pentoxide and into a cold trap at -20°C., where most of the nitrogen dioxide condenses. The product so formed should not be contaminated by nitric oxide, which when present forms nitrous anhydride and gives a green or blue product. Dissolved oxygen is removed by repeated low-pressure distillation (117).

C. FROM NITROUS AND NITRIC ANHYDRIDES

A practically convenient and theoretically interesting method is the reaction of dinitrogen trioxide (N_2O_3) with dinitrogen pentoxide (N_2O_5). Concentrated nitric acid distilled with arsenious oxide and concentrated sulfuric acid yields nitrous anhydride (N_2O_3) mixed with some nitrogen dioxide; a mixture of nitric acid and phosphorus pentoxide behaves as dinitrogen pentoxide. When these constituents are mixed, nitrogen dioxide is evolved (326, 327):

$$N_2O_3 + N_2O_5 \rightarrow 2N_2O_4 \rightleftharpoons 4NO_2$$

D. FROM THE NITROSYL ION AND THE NITRATE ION

Partington recommends (296), as the best laboratory method of preparing nitrogen dioxide, the reaction between potassium nitrate and nitrosyl bisulfate which was discovered (294) by Girard and Pabst in 1878.

$$KNO_3 + NOHSO_4 \rightarrow KHSO_4 + N_2O_4$$

i.e.

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

It represents the reverse of the self-ionization of dinitrogen tetroxide.

E. FROM NITRIC OXIDE AND OXYGEN

Though convenient on a laboratory scale, none of the previous methods is industrially important. On the large scale nitrogen dioxide is made from nitric oxide by oxidation with air; the nitric oxide itself comes from the nitrogen and oxygen of the air, either directly or *via* the catalytic synthesis and oxidation of ammonia.

$$2NO + O_2 \rightarrow 2NO_2$$

This reaction has been investigated experimentally for many years (68) and is of great technical importance. Its characteristics will be outlined here because of its theoretical interest and for the light it throws on the chemistry of nitrogen dioxide. It has two striking properties: (*1*) it is kinetically a third-order reaction; (*2*) the velocity constant, k, decreases with increasing temperature (57, 58).

Three principal types of solution to the problem have been advanced: (*1*) on the collision theory, just as binary collisions can be shown to be the basis of second-order, bimolecular reactions, so it is suggested that ternary collisions can explain this third-order one; (*2*) the transition-state theory attempts to examine the path which the reaction follows in its course from reactants to products; (*3*) consecutive bimolecular reactions have also been invoked to explain third-order characteristics.

1. Triple collisions in the reaction $2NO + O_2 \rightarrow 2NO_2$

The simple kinetic theory of gases based on a model of rigid spherical molecules implies a definite frequency of binary encounters in a gas, but without further assumptions cannot yield a value for the rate of ternary encounters. The difficulty lies in the definition of what constitutes a triple collision. In 1922 Bodenstein (58) suggested that the relative frequencies of ternary and binary collisions were in the ratio of molecular diameter (σ) to mean free path (λ), or 1:1000 in a light gas at normal temperature and pressure. He pointed out that for a reaction to proceed at low temperatures at an appreciable rate *via* ternary collisions it must have a small activation energy. This approach may be interpreted as implying a finite duration, τ, to every encounter. Herzfeld and Steiner developed this concept (194, 379) and calculated a formula for the frequency of binary collisions which was further developed by Rabinowitch (321). In the application of ternary collision theory to this oxidation of nitric oxide we readily account for the third-order characteristics; the decrease of rate constant with temperature implies a further requirement—the lifetime τ diminishes as the temperature rises.

2. Transition-state theory of the reaction $2NO + O_2 \rightarrow 2NO_2$

This theory differs from the collision theory in several ways. Basically its assumptions require that the reactants associate to form a complex containing sufficient energy to react. The complex is supposedly in equilibrium with the reactants; if certain (reasonable) assumptions are made about the nature of the complex, its concentration and its rate of reaction may be inferred. An elegant description of the oxidation of nitric oxide has been given in these terms (147, 155). The description may be summarized in the predicted relation

$$10^{-16}k_3\ (\text{cc.}^2\ \text{mole}^{-2}\ \text{sec.}^{-1}) = g_\ddagger \overset{7}{\Pi}\,(1 - e^{-h\nu_\ddagger/kT})^{-1}/T^3$$

where $\nu_\ddagger$ represents the vibration frequencies of the activated complex and $g_\ddagger$ represents the electronic multiplicity of the activated complex. $g_\ddagger$ must lie between 1 (N_2O_4) and 28 ($2NO + O_2$), and is assumed to be 4 ($2NO_2$).

The value zero is obtained experimentally for the activation energy. Then the rate as a function of temperature is calculated. It decreases with temperature initially because of the factor T^{-3}, passes through a shallow minimum, and rises again as the influence of the terms in ν is felt. The minimum value (155) occurs close to the experimental minimum (68).

3. Successive bimolecular steps in the reaction $2NO + O_2 \rightarrow 2NO_2$

All the species concerned—nitric oxide, oxygen, and nitrogen dioxide—are free radicals, and evidence of dimerization has been found in each system. To avoid the uncertainties of ternary collisions of variable duration it has been suggested that reaction proceeds through an unstable intermediate association compound. Two schemes may be set out in terms of $(NO)_2$ or of NO_3:

$2NO \rightleftharpoons (NO)_2$ K; mobile equilibrium, rapidly established

$(NO)_2 + O_2 \rightarrow 2NO_2$ k_2; rate-determining step

The dimer $(NO)_2$ has been detected in solid, liquid, and gaseous nitric oxide by magnetic, calorimetric, and x-ray studies.

This pair of equations would imply:

$$\frac{d[NO_2]}{dt} = k_2K[NO]^2[O_2] \qquad \text{i.e., } k_3 = k_2K$$

with the temperature dependence of k_3 attributed to the fall of K with temperature.

The alternative scheme has also been considered (403):

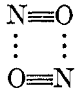
$NO + O_2 \rightleftharpoons NO_3$ K'; mobile equilibrium rapidly established

$NO_3 + NO \rightarrow 2NO_2$ k_2'; rate-determining step

It leads to the equation

$$\frac{d[NO_2]}{dt} = k_2'K'[NO]^2[O_2] \qquad \text{i.e., } k_3 = k_2'K'$$

The two schemes are very similar. Currently, the NO dimer is supposed to be a square complex



The NO_3 may either be similar to $(NO)_2$, or it may be the pernitrite (ONOO) or the nitrate radical. There is evidence for the oxidation of nitric oxide by the nitrate radical in the decomposition of dinitrogen pentoxide and for the existence of the pernitrite radical from the recent work on isotopic exchange (285).

The model of the transition-state theory is closest to the pernitrite-nitric oxide complex.

III. THE EQUILIBRIUM $N_2O_4 \rightleftharpoons 2NO_2$

Numerous experimental methods have been used to determine the composition of the equilibrium mixture in the gaseous, liquid, and solid states; recently kinetic measurements have been made to determine the rate of attainment of equilibrium in the gas phase.

A. EQUILIBRIUM IN THE GAS PHASE

1. Experimental investigations

The degree of dissociation, α, in the gas phase may be derived from measurements of density, D, and pressure, P, or from measurements of pressure and volume, V.

Species:	N_2O_4	$\rightleftharpoons 2NO_2$	Total
Moles:	$(1-\alpha)n$	$(2\alpha)n$	$(1+\alpha)n$

$$(PV)_{\text{obs.}} = (1+\alpha)nRT$$

Thus

$$\alpha = \frac{PV}{nRT} - 1 = \frac{MP}{DRT} - 1$$

where n represents the total number of moles present expressed as N_2O_4, and $M = 92.016$ is the molecular weight of N_2O_4. These formulas apply to ideal gases. Small deviations from ideality may be allowed for by the term λ in the equation

$$PV = RT(1 + \lambda P) \text{ for each species}$$

Three outstanding sets of measurements have been made (59, 411, 433). Their consistency and their relation to previous data (60, 268, 269) have been assessed (149). The results are most conveniently expressed in terms of the equilibrium constant:

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

Bodenstein and Boes (59) assumed that in their work at pressures from 0.25 to 0.75 atm. deviations from ideality according to the modified gas equation $PV = RT(1 + \lambda P)$ could be satisfactorily represented by $\lambda_{NO_2} = \lambda_{CO_2}$ and $\lambda_{N_2O_4} = 2\lambda_{NO_2}$. They summarized their results in the equation:

$$\log_{10} K_p \text{ (mm.)} = -2692/T + 1.75 \log T + 4.83T/10^3 - 7.144T^2/10^6 + 3.062$$

Verhoek and Daniels (411) worked at pressures above and below 1 atm. They allowed for gas imperfections in a similar way by setting $\lambda_{N_2O_4} = 2\lambda_{NO_2}$; for λ_{NO_2} they took λ_{SO_2}. They expressed their results in a form showing clearly the influence of gas imperfections:

$$\begin{aligned} \text{At } 298.2°\text{K.} \quad K_p(\text{atm.}) &= 0.1426 - 0.7588\, C_0 \\ 308.2 \quad &= 0.3183 - 1.591\, C_0 \\ 318.2 \quad &= 0.6706 - 3.382\, C_0 \end{aligned}$$

C_0 denotes the total concentration expressed as *moles of dinitrogen tetroxide per liter.*

2. Thermodynamic functions for individual species NO_2 *and* N_2O_4

Excellent values for the principal thermodynamic functions of the gaseous equilibrium were derived from these and other data by the application of the third law of thermodynamics (149):

Equilibrium	ΔH^0_0	$\Delta H^0_{298.16}$	$\Delta S^0_{298.16}$	$\Delta F^0_{298.16}$
$N_2O_4 \rightleftharpoons 2NO_2$	12,875 cal.	13,693 cal.	42.21 cal. degree^{-1}	1110 cal.

As a result of this work precise values are also available for the entropies and free-energy functions $(F - H^0_0)/T$ of the individual species. The actual enthalpies and free energies of formation, however, still rest on experimental work which, though very good, is also very old (48, 49) and may thus be subject to some uncertainty. Table 1 lists the principal thermodynamic functions.

TABLE 1

Thermodynamic functions for gaseous NO_2 *and* N_2O_4 *at 298.16°K. and 1 atm.*

Function	NO_2	N_2O_4
$S^0_{cal.}$ (cal. deg.$^{-1}$ mole^{-1})	57.47	72.73
$S^0_{abs.}$ (cal. deg.$^{-1}$ mole^{-1})	59.65	77.10
ΔS^0_f (cal. deg.$^{-1}$ mole^{-1})	−14.46	−71.12
$-(F^0 - H^0_0)/T$ (cal. deg.$^{-1}$ mole^{-1})	49.202	59.106
ΔH^0_f (cal. mole^{-1})	7,964	2,239
ΔF^0_f (cal. mole^{-1})	12,275	23,440

B. EQUILIBRIUM IN THE LIQUID AND SOLID PHASES

1. Ideal solution

If the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ is established in an ideal solution, then the gases above the solution are also in equilibrium. If they, too, are ideal, then:

$$K_c \text{ (solution)}/K_c \text{ (gas)} = (P^0_{N_2O_4}/P^{0\,2}_{NO_2})(RT/V_0)$$

where K_c are equilibrium constants in moles per liter, V_0 is the volume per mole of solution, and the P^0's are the (hypothetical) vapor pressures of the individual species in the liquid state.

Thus at a given temperature (K_cV_0) solution should be a constant for a set of ideal solvents (145, 266, 292), while

$$\Delta H \text{ (solution)} - \Delta H \text{ (gas)} = L_{N_2O_4} - 2L_{NO_2}$$

The relative velocities of the two reactions are thus altered to this extent, but whether the rate of dissociation or that of combination or both are affected cannot be decided.

2. Real solutions

Colorimetric techniques have been used (105, 106, 107, 266) to measure the fractional dissociation and its dependence on temperature in a number of organic solvents. In every case K_c (solution) $<$ K_c (gas) and ΔH (solution) $<$ ΔH (gas), although none of the solutions could be called ideal. Moelwyn-Hughes presents Cundall's figures, as shown in table 2.

3. Pure liquid

The pure liquid appears to contain very little of the NO_2 species. From measurements of magnetic susceptibility Soné (374) concludes that the pure liquid contains 0.7 per cent nitrogen dioxide.

TABLE 2

The influence of solvent on the equilibrium constant

K_c *(mole liter*$^{-1}$*)* $= [NO_2]^2/[N_2O_4]$ *at 20°C.*

Solvent	K	ΔH^0	$\Delta H^0_{\text{soln}} - \Delta H^0_{\text{gas}}$
	mole liter^{-1}	*cal.*	*cal.*
Gas phase	382	13,693	
$SiCl_4$	17.8	20,470	6780
CS_2	13.3	19,400	5710
CCl_4	8.05	18,840	5150
$CHCl_3$	5.53	21,210	7520
C_2H_5Br	4.79	20,490	6800
C_6H_5Br C_6H_5Cl	3.70	19,350	5660
C_6H_6	2.23	22,180	8490

4. Pure solid

The solid is assumed to contain only dinitrogen tetroxide. It is diamagnetic and colorless.

C. THE RATE OF ATTAINMENT OF THE EQUILIBRIUM $N_2O_4 \rightleftharpoons 2NO_2$ IN THE GAS PHASE

At normal temperatures equilibrium in a mixture of nitrogen dioxide and dinitrogen tetroxide is established too rapidly for conventional methods of chemical kinetics to be applied. Thermodynamics, however, determines the ratio of the rates of association and dissociation, and the difference in activation energies:

$$N_2O_4 \rightarrow 2NO_2 \qquad k_d \qquad E_d = RT^2(\mathrm{d} \ln k_d/\mathrm{d}T)$$

$$2NO_2 \rightarrow N_2O_4 \qquad k_a \qquad E_a = RT^2(\mathrm{d} \ln k_a/\mathrm{d}T)$$

$$k_d/k_a = K_c \qquad E_d - E_a = \Delta H - RT$$

The accurate thermodynamics of equilibrium developed in Section V are essential to the interpretation of all attempts to measure the kinetic parameters.

The first attempts (172, 217, 334, 367) were based on a theory, due to Einstein, of the dependence of the speed of sound in a dissociating gas on its frequency. Unfortunately, measurements of this type are sensitive both to impurities and to adsorption, and the corrections which have to be applied for gas imperfection are large. Measurements of absorption of sound are essential; for precise work they need to be accurately made over a considerable frequency range (222, 390). However, careful assessment (222) of the best of the dispersion measurements (334) allows limits to be set to the possible values of k_d, the first-order rate constant of dissociation:

$$\text{At } 0°\text{C. } 3 \times 10^4 < k_d\ (\text{sec.}^{-1}) < 4 \times 10^5$$

$$\text{At } 25°\text{C. } k_d\ (\text{sec.}^{-1}) \sim 7 \times 10^4$$

A steady-state flow system, in which a mixture of nitrogen dioxide and dinitrogen tetroxide was subjected to a discontinuous pressure change, was used to overcome some of the previous difficulties. Temperature measurements were used to follow the return of the system to equilibrium (66). A lower limit of k_d (sec.$^{-1}$) $> 8.2 \times 10^4$ was found at 1 atm. and 25°C. The chief difficulty of all these methods is that the dissociation of even as simple a gas as dinitrogen tetroxide is not a single process. Unless concentrations of individual species are determined as a function of time, any detected variable must be arbitrarily identified with a particular combination of processes, and this identification may be difficult.

Recently, determinations (40, 79) have been made which do reduce some of the difficulties.

In one (79) a very weak shock wave passing through the mixture causes a very rapid, adiabatic compression and a sharp entropy change, and raises the temperature of the gas. The rate of attainment of equilibrium corresponding to this new temperature is followed photometrically (in such a way as to eliminate relaxation processes which arise from energy transfers between vibration and translation). In the presence of an excess of nitrogen (total pressure = 1 atm.; temperatures from −20°C. to +28°C.) the dissociation followed second-order kinetics (equation 3a):

$$d[N_2O_4]/dt = k_d'[N_2][N_2O_4] \tag{3a}$$

with $k_d' = 2 \times 10^{14} \exp(-11{,}000/RT)$ liter mole^{-1} sec.$^{-1}$, while the limiting first-order rate constant $k_d = 10^{16} \exp(-12{,}900/RT)$ sec.$^{-1}$ Thus at 25°C. $k_d = 6.4 \times 10^4$ sec.^{1}

In the other method (40) a steady-state system is used. A stream of $NO_2 + N_2O_4$ is subjected to an almost instantaneous (10^{-3} μ sec.) compression. Enthalpy is supplied over a period ranging from 1 m. sec. to 1 μ sec. The quantity measured —a net entropy gain—is not a single concentration change but is characteristic of the system as a whole; all relaxation processes are involved and their roles must be assessed. It is found, on the present evidence, that molecules of nitrogen and molecules of dinitrogen tetroxide are not very different in efficiency of transferring energy.

The results of these two (40, 79) modern methods are in substantial agreement (189). They are expressed below in terms of relaxation time, τ, to equilibrium at 25°C. as a function of pressure, p.

Pressure (atm.)	0.27	0.47	0.65	1.0
Relaxation time (μ sec.)	0.71	0.38	0.24	0.14

From the first-order dissociation rate constant and the equilibrium constant the second-order association rate constant may be shown to be 5.2×10^8 l. mole^{-1} sec.$^{-1}$ at 25°C. If the activation energy of association E_a is assumed zero and the molecular diameter σ_{NO_2} set at 4.6 Å., then the steric factor in $k_a = PZ_2 \exp(-E_a/RT)$ is $P = 5 \times 10^{-3}$.

IV. PHYSICAL PROPERTIES OF THE EQUILIBRIUM MIXTURE

Solid, liquid, and gaseous systems will be considered in succession, and it will be seen that the mobile equilibrium makes its influence felt in the gaseous state. Much old work (up to 1935) is listed in Gmelin's (156) excellent German text and is referred to only briefly here. In recent times the work of Giauque and Kemp (149) on thermodynamic properties, of Sage (332, 335) on volumetric behavior, and of Addison (5, 6) on electrical properties is noteworthy.

A. SOLID NITROGEN DIOXIDE

At low temperatures nitrogen dioxide is a colorless solid. Between −30°C. and −20°C. it is pale lemon-yellow; at the melting point (−11.2°C.) it is honey-colored (156). X-ray powder photographs taken at liquid-air temperatures (191, 409, 410) show that it is a body-centered cubic lattice with twelve NO_2 or six N_2O_4 molecules in the unit cell. Studies on single crystals at −40°C. confirm this and give for the size of the unit cell a = 7.77 ± 0.01 Å. (70), corresponding to a density of 1.95 g. cc.$^{-1}$ The density of the solid has been recorded by previous workers (55, 156) as the result of direct measurements (262) and of x-rays (55, 409).

Temperature	−253°C.	−195°C.	"Liquid air"	−79°C.	−40°C.
Density (g. cc.$^{-1}$)	2.0	1.981	1.94	1.902	
		1.976	1.942	1.896	1.95

The expansion coefficient (α) of the solid, calculated as a mean coefficient of cubical expansion between −79°C. and −195°C., is 3.6 × 10^{-4}°C.$^{-1}$

The specific heat, C_p, has been measured from 16.80°K. to near the melting point (149). It increases monotonically without any transitions occurring in the solid. At the melting point C_p is 26.51 cal. deg.$^{-1}$ (mole N_2O_4)$^{-1}$. The change of 6.14 in the molar specific heat on melting (from 26.51 to 32.65 cal. deg.$^{-1}$ mole^{-1}) implies that new degrees of freedom other than translation, which can account for only 3 cal. deg.$^{-1}$ mole^{-1}, have come into play. However, the Raman spectra of the liquid and the solid are the same (262).

The vapor pressure of the solid from 240.3°K. to 261.90°K. (149) may be represented by the equation:

$$\log_{10} P \text{ (int.cm.Hg)} = -2460.000/T + 9.58149 + 7.6170T/10^3 + 1.51335T^2/10^5$$

The triple point is 261.80°K. (−11.2°C.) (149); at this point the vapor pressure above the system is 13.978 int. cm. of mercury. The latent heat of fusion (measured electrically) is 3502 ± 3 cal. mole^{-1}; the entropy of fusion is 13.37 cal. deg.$^{-1}$ mole^{-1}.

These values lead to a cryoscopic constant K_f (= molar freezing-point depression per 100 g. of dinitrogen tetroxide) of 48° against the experimental value of 41° (73, 324, 325).

The dielectric constant (ϵ) of solid dinitrogen tetroxide at −40°C. was found to be 2.6 (355).

B. LIQUID NITROGEN DIOXIDE

Liquid nitrogen dioxide darkens from a yellow color at low temperatures as the temperature is raised. (Impure specimens are often colored green, owing to the presence of small amounts of nitrous anhydride.) Nitrogen dioxide can be strongly supercooled below its triple point (−11.2°C.). Vapor pressure measurements have been made down to −110°C. It can exist as a liquid up to the critical temperature, 158°C.

The density of the liquid has been measured as a function of temperature by various workers (45, 64, 263, 303, 351, 396). The most complete modern work is that of Reamer and Sage (332), who have measured the specific volume of the liquid as a function of temperature and pressure from 22°C. to the critical temperature. At 0°C. the density is 1.4905 g. cc.$^{-1}$; by 20°C. it is 1.447. The specific volume (cc. g.$^{-1}$) has been measured between 0° and 20°C. and has been expressed (64) by the formula:

$$V_{t^\circ\text{C.}} = 0.67037 + 10.075(t/1000) + 3(t/1000)^2$$

The specific heat (cal. deg.$^{-1}$ mole^{-1}) of the liquid increases from 32.65 at the triple point to 33.9 at the normal boiling point, 21.15°C. (149).

The vapor pressure of the (supercooled) liquid has been measured as follows: down to −110°C. (330, 351); between the triple point and the normal boiling point (149) with great precision; and up to the critical temperature (263, 350, 352).

Typical values are given below:

Temperature	Vapor Pressure	Temperature	Vapor Pressure
°C.	*mm.*	*°C.*	*mm.*
−100*	1.1*	0.84	266
−80	5.3	10	454
−25	70	15	569.4
−11.2	139.8	21.15	760.0

* For the supercooled liquid.

In the temperature range 261.9° to 294.9°K. (149) the equation:

$$\log_{10} P \text{ (int.cm.Hg)} = -1753.000/T + 8.00436 - 11.8078T/10^4 + 2.094T^2/10^6$$

holds with accuracy.

High-pressure results (up to 120°C.) have been represented by the equation:

$$\log p \text{ (mm. Hg)} = -1325.6/T + 3.354 \log T - 0.8950$$

though the tabulated results of Schlinger and Sage are to be preferred. A tabulation is given below:

Temperature	Saturation Vapor Pressure	Temperature	Saturation Vapor Pressure
°F.	*p.s.i.a.*	*°F.*	*p.s.i.a.*
100	30.69	250	543.9
150	91.06	300	1160.1
200	235.01	316.8	1469.0

Under atmospheric pressure liquid nitrogen dioxide boils at 294.25°K. (21.15°C.). The calorimetrically measured latent heat of vaporization at the boiling point is 9110 ± 9 cal. mole^{-1} (149); the difference between this value and that calculated from the Clausius–Clapeyron equation is small. The molecular elevation of the boiling point (100 g. of solvent) is 13.7°C. (138, 140). The standard entropy of vaporization at the normal boiling point is 30.96 cal. (deg. mole N_2O_4)$^{-1}$. (This high value reflects the change in the degree of dissociation in liquid and gas.)

Critical constants have been measured recently (332) and *P-V* isotherms of dinitrogen tetroxide in the neighborhood of the critical point accurately mapped.

The critical constants are $T_k = 158.2°\text{C.}$, $P_k = 99.96$ atm., and $V_k = 165.3$ cc. mole^{-1}. These confirm previous determinations (45, 350, 351) and diminish the uncertainty.

It is interesting to note that $T_b = \frac{2}{3}T_k$ closely. The volume of the solid at absolute zero is 46 cm.^{3} (*cf.* $165.3 = V_c$).

The surface tension, γ, of the liquid at 20°C. is 26.5 ergs cm.$^{-2}$ (156) and the molar surface energy, $\gamma V_M^{2/3}$, is 423.5 ergs (328, 329, 351).

The viscosity, η (in dynes sec. cm.$^{-2}$), of the liquid has been recently remeasured (335) over a range of temperatures (40°F. to 280°F.) and pressures (1 atm. to 330 atm.), confirming and extending previous work (38a, 397, 399). It is found that η varies only slowly with pressure. Typical values of η are given below:

t (°C.)	0	10	20		
$10^3\ \eta$ (poises)	5.275	4.68	4.18		
T (°F.)	40	100	160	220	280
p (p.s.i.a.)		30.7	111.2	332.8	864.1
$10^6\ \eta$ (poises)	4990	3420	2235	1325	570

Various formulas have been suggested to represent the temperature dependence; e.g.

$$\eta\ (\text{poises}) = 28.155/(140.89 + t)^{1.7349}$$

t is given in °C.

Electrical and optical properties have recently been remeasured (5). Liquid nitrogen dioxide has been recognized as a poor conductor of electricity since the first measurements of its electrical conductivity by Faraday (129); the conductivity σ increases with temperature, as the data below indicate:

T (°C.)	7.3	13.6	19.5	20.4
$10^{12}\sigma$	1.17	1.71	2.19	2.24

The temperature coefficient of resistance $(1/R)(\mathrm{d}R/\mathrm{d}t)$ is 8.5×10^{-14} ohm cm.$^{-1}$ deg.$^{-1}$ (5). These measurements completely supersede previous work.

The dielectric constant, ϵ, of the liquid at 15°C. is 2.42, corresponding to a molar polarization $P = 26.5$ cc. (6).

The refractive index has been measured (6) as a function of wavelength, and the Cauchy formula

$$n_\lambda = n_\infty + a/\lambda^2$$

has been used to derive n_∞ and from it the molar refractivity. The values found are as follows:

λ	4358.3	4916.4	5460.7	5893	∞
n_λ	1.442	1.431	1.424	1.420	1.394

These correspond to a molar refractivity $R_\infty = 15.2$ cc.

Solubilities in liquid nitrogen dioxide parallel those in diethyl ether; because of its low dielectric constant it is not a good ionizing solvent and in it carboxylic acids are associated. In general it may be stated that no inorganic salts dissolve in it. Because of its reactivity, numerous compounds which are dissolved by liquid nitrogen dioxide may also undergo some reaction. The dinitrogen tetroxide solvent system is considered in more detail in Section VIII.

C. GASEOUS NITROGEN DIOXIDE

The saturation vapor pressure of nitrogen dioxide has been measured from −110°C., when it is 1 mm. of mercury, up to 158°C., when it is 100 atm.; already at 150°C. decomposition to nitric oxide and oxygen is apparent and by 600°C. it is complete. These temperatures limit the effective range over which the vapor has been quantitatively studied. At the normal boiling point (21.15°C. at 76.00 cm.) the vapor is brown. As the temperature is raised and the proportion of nitrogen dioxide is increased, it darkens. At 150°C. it is black.

1. Equation of state; density; expansion and compressibility coefficients

The gas density has been measured directly by numerous workers (156); especially careful work was done by Natanson and Natanson in 1885–86 (268, 269). The different measurements were correlated by Giauque and Kemp (149). Densities derived from combined data summarized in terms of equilibrium constants are, at low pressures, more reliable than any single set of results. These remarks are equally true of the measurements made on the saturated vapor (45, 351). The most recent determinations comprise values of the specific volume of the gaseous system for temperatures from 22°C. to 165°C. and for pressures up to 400 atm. The results of these measurements are presented as tables and graphs of specific volumes and compressibility factors (352).

For common purposes the effect of the mobile equilibrium far outweighs gas imperfections. However, equations of the form $PV = RT(1 + \lambda P)$ have been used at relatively low pressures for each of the species present (59, 411) and equations of state have been proposed for the mixture in terms of pressure and density (25a) or in the form of the van der Waals equation with values of a and b derived from critical data (350). In all the aspects of the behavior of the gas the shifting equilibrium makes itself felt.

The expansion coefficient, $\alpha = (1/V)(\partial V/\partial T)_p$, at 1 atm. passes through a maximum at 40°C. as the temperature changes (112, 113):

t (°C.)	26.7	35.4	39.8	49.6	60.2	70.0	80.6	135
$10^5\ \alpha$ (°C.$^{-1}$)	888	1008	1215	1207	1137	946	781	367

By 135°C. it has the value 0.00367 deg.$^{-1}$, characteristic of an ideal gas.

The expansion coefficient and compressibility have been explicitly related (382).

2. Specific heat, thermodynamic functions, thermal conductivity

The specific heat at constant pressure of the equilibrium mixture shows a similar maximum (50, 51, 52, 247) at about 62°C. It is another consequence of the dissociation equilibrium, and the theory of the effect has been worked out by Eucken (126). This is the reason for the otherwise astonishing specific heat values quoted in tables. If α is the fraction dissociated and ΔH the heat of dissociation, then:

$$C_p = C_p^{N_2O_4} + \alpha[2C_p^{NO_2} - C_p^{N_2O_4}] + \alpha(1 - \alpha^2)\Delta H^2/2RT^2$$

The ratio C_p/C_v has been measured both by the method of Clement and Desormes and by measurements on the speed of sound. For pure nitrogen dioxide the value $\gamma = 1.31$ may be extrapolated.

The thermodynamic functions for the equilibrium mixture of gaseous nitrogen dioxide at its normal boiling point were part of the primary experimental data of Giauque and Kemp and have been discussed in Section III.

The thermal conductivity k in cal. (cm. sec. deg.)$^{-1}$ varies with the temperature, passing through a maximum at about 65°C. (131, 252, 253). By representing the conductivity k as the sum of two contributions, k_1 due to the separate constituents of the mixture and k_2 due to the effect of altering the equilibrium, Nernst (270) was able to derive an explicit formula for k_2:

$$k_2 = \Delta H^0 \frac{DP}{RT^2}\left(1 - \frac{RT}{\Delta H}\right)\left(1 - \frac{\Delta H}{RT}\right)\frac{\alpha(1 - \alpha^2)}{(1 + \alpha)^2}$$

3. Optical and electrical properties

The refractive index of the vapor (108, 121) has been split into contributions from the separate constituents:

$$NO_2,\ n = 1.000509;\ N_2O_4,\ n = 1.001123$$

The dielectric constant of the gaseous equilibrium mixtures has been measured by a number of workers, and although the older measurements are not very precise, all the results are in substantial agreement (37, 148, 424, 425, 439) and undoubtedly the most authoritative is that of Schultz (359). Completely different interpretations have been advanced to explain the dependence of the dielectric constant on temperature and pressure in terms of the two species. On one view (37, 148, 424) dinitrogen tetroxide is assigned zero dipole moment; this requires that nitrogen dioxide should have a finite dipole moment diminishing rapidly with temperature. The other view (349, 359) rejects temperature-dependent dipole moments and instead suggests that both nitrogen dioxide and dinitrogen tetroxide have finite dipole moments of 0.286 and 0.371 D, respectively. The arguments advanced (359) in support of the latter view command more respect. A different opinion based on a selection of the controversial points has recently been expressed (19).

The absorption of light by the gaseous equilibrium mixture is discussed in Section VII,E under the photolysis of nitrogen dioxide. Dinitrogen tetroxide is transparent to wavelengths in the visible; nitrogen dioxide absorbs very strongly throughout the visible range.

4. Adsorption of gaseous nitrogen dioxide

In its manufacture from the oxidation of nitric oxide by air nitrogen dioxide is, of course, formed in the presence of an excess of nitrogen. Among proposed methods of concentrating it have been its adsorption on and regeneration from various active surfaces. This has stimulated research into its adsorption on numerous surfaces—glass, active carbon, silica gel. Glass (159) becomes covered with a monolayer of nitrogen dioxide at room temperatures and pressures of 0.5 to 1 mm. of mercury. Active carbon at 20°C. absorbs some 28 per cent of its own weight of nitrogen dioxide; desorption at 150°C. is accompanied by some oxidation of the carbon (360). The heat of adsorption on silica gel varies from 4600 to 7500 cal. per mole of N_2O_4 (383); the isotherm has the classical form (331). A systematic study has been made of both its adsorption from its mixtures with air (288, 331, 360, 378, 383) over a range of temperatures and pressures and its desorption by a stream of hot air (331) or by heating (378).

V. Physical Properties of the Individual Species (NO_2, N_2O_4)

Some of the physical properties considered in Section IV are conveniently described in terms of the equilibrium mixture. It is more convenient, however, to deal with some other physical properties in terms of the individual species.

A. NITROGEN DIOXIDE MONOMER

1. Paramagnetism

Nitrogen dioxide is an odd-electron molecule (seventeen "valency" electrons) and is paramagnetic. The paramagnetism gives to nitrogen dioxide a volume susceptibility $\chi = 3 \times 10^{-15}$ c.g.s. units (190), in good agreement with the quantum theory prediction (412) for a magnetic moment due only to one electron:

$$\chi_M = \frac{4(N\mu_0)^2 S(S+1)}{3RT} + N\alpha$$

in terms of $O_2 = \chi_M(NO_2)/\chi_M(O_2) = 0.390$, the theoretical value being 0.375. Thus the quantum numbers $J = S = \frac{1}{2}$ and $L = 0$, and the ground state is designated $^2\Sigma$.

The electronic multiplicity of g is given by the general formula and the contribution to the entropy is R ln 2.

$$g = 1 + \{S(S+1) + J(J+1) - L(L+1)\}/2J(J+1) = 2$$

This g-factor enters both the transition-state theory of nitric oxide oxidation (147) (and nitrogen dioxide decomposition) and the statistical calculation (149) of entropy.

2. Ionization potential and electron affinity

Different values have been reported for the ionization potential of nitrogen dioxide (318, 373). Kandel (213a) has recently obtained a value of 9.91 e.v. (228.5 kcal.) from appearance potential studies using nitromethane.

The electron affinity of nitrogen dioxide has been derived from empirical though consistent values of the lattice energies of the nitrites as 1.62 e.v. (37.3 kcal.) (320).

3. Bond lengths and angle

Nitrogen dioxide is an isosceles triangle. The side (N—O) = 1.188 ± 0.004 Å.; the ONO angle is 134° 4′ ± 15′ (71, 267). These values come from recent infrared measurements in the 1.4 to 3.4 μ region; they lie within the limits of the best existing electron diffraction (88) data, which give 1.20 ± 0.02 Å. and 132 ± 3° and yield a value for the product $I_1I_2I_3$ of the principal moments of inertia of 1.44×10^{-116} g.^{3} cm.^{6}, in agreement with thermodynamic data (149). These values do not support the assignment made in recent microwave studies (246).

4. Vibration frequencies

Although the fundamental frequencies were assigned correctly on the basis of observations in the ultraviolet (179, 181), two of the three fundamentals have been observed for the first time only recently (428). The observed fundamental frequencies (cm.$^{-1}$) are: $\nu_1 = 1322.5 \pm 0.2$ (symmetrical stretching), $\nu_2 = 750.9 \pm 0.4$ (bending), and $\nu_3 = 1616.0 \pm 0.2$ (asymmetrical stretching).

The six anharmonicity constants have also been listed: $\chi_{11} = 7.1$, $\chi_{12} = 16.0$, $\chi_{13} = 33.4$, $\chi_{22} = 8.1$, $\chi_{23} = 8.2$, $\chi_{33} = 15.9$, and the zero-order frequencies (cm.$^{-1}$) deduced: $\omega_1 = 1361.4 \pm 1.7$, $\omega_2 = 770.2 \pm 6.6$, $\omega_3 = 1668.6 \pm 1.7$.

5. Thermodynamic functions for nitrogen dioxide

As a result of the work of Giauque and Kemp (149) precise values are available for the entropies S^0 and free-energy functions $(F^0 - H_0^0)/T$ of nitrogen dioxide. These were actually based on the accurate data available on the $2NO + O_2 \rightleftharpoons 2NO_2$ equilibrium (60). They are in close agreement with values which can now be calculated from formulas of statistical mechanics such as the equation:

$$(F^0 - H_0^0)/T = -\frac{3}{2}R \ln M - 4R \ln T - \frac{R}{2} \ln I_1I_2I_3 - R \ln g + R \ln \sigma - 257.401 + \sum_{i=1}^{3} (F_i^{\text{vib}}/T)$$

and, in fact, Giauque and Kemp used this equation to deduce a value of $I_1I_2I_3$, the product of the principal moments of inertia being not then known. The actual 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 (48, 49). The principal thermodynamic functions are listed in table 1.

6. Dipole moment of nitrogen dioxide

As the molecule is angular it is expected to possess a non-zero moment. Knowledge of this dipole moment depends on the interpretation of dielectric constant measurements on the equilibrium mixture at different temperatures (see Section

IV,C,3). All recent experimenters are agreed that this lies between 0.58 and 0.28 Debye units. Two opinions exist: (*1*) that it is constant and equal to 0.286 D (358), and (*2*) that it is dependent on temperature and varies from 0.3 at 125°C. to 0.58 at 25°C. (424). This calculation of the temperature-variable dipole moment contains serious inconsistencies, but permits a zero moment for dinitrogen tetroxide The other calculation (425) is self-consistent, though it implies a non-zero dipole moment for dinitrogen tetroxide.[3]

B. DINITROGEN TETROXIDE

1. Diamagnetism of dinitrogen tetroxide

Dinitrogen tetroxide has an even number of electrons and is diamagnetic (190, 300, 301, 374). The most recent determination of the molecular susceptibility is $\chi_M = -30 \times 10^{-6}$ C.G.S. units (374).

2. Bond lengths and angles in dinitrogen tetroxide

The structure of dinitrogen tetroxide is considered in Section VI,B.

3. Vibration frequencies in dinitrogen tetroxide

The spectrum of the equilibrium mixture is extraordinarily rich in lines, and assignment of the twelve possible fundamental frequencies is still not undisputed. The older data have been summarized by Sutherland (381) and by Harris and King (180). Work on infrared absorption (305, 429) and Raman spectra (240, 261) is still in progress. One assignment that has been suggested is (427):

$$\nu_1 = 1334;\ \nu_2 = 811;\ \nu_3 = 265;\ \nu_4 = 160;\ \nu_5 = 1722;\ \nu_6 = 320$$

$$\nu_7 = 684;\ \nu_8 = 500;\ \nu_9 = 1747;\ \nu_{10} = 430;\ \nu_{11} = 1240;\ \nu_{12} = 748$$

The work of Giauque and Kemp, which assumed *one* classically excited vibration, gave excellent agreement between theory and experiment and is evidence against any internal rotations.

4. Thermodynamic functions for dinitrogen tetroxide

The principal thermodynamic functions for dinitrogen tetroxide are listed in table 1. In the evaluation of these quantities the starting points were the calorimetrically measured entropy of a mixture of gaseous nitrogen dioxide and dinitrogen tetroxide, the calculated entropy of pure gaseous nitrogen dioxide, and the composition of the mixture. These permitted calculation of the entropy, S^0, of dinitrogen tetroxide. From S^0 and an assumed assignment of vibration frequencies, including one very low frequency with (classical) energy kT, an expression for

$$\Delta\left(\frac{F^0 - H_0^0}{T}\right)_{N_2O_4 \rightarrow 2NO_2}$$

---

[3] The origin of this conflict may lie in the size of the atomic contribution to the total polarization P. For a molecule with a long nitrogen–nitrogen distance this may be exceptionally large.

was obtained. This expression could be reconciled with all the experimental data (*viz.* $\Delta F^0/T$) by one very precise value of ΔH^0_0; this satisfactory solution confirmed the basic correctness of the assumed single classical frequency and definitely excludes free rotation, for example, of the NO_2 groups.

6. Dipole moment of dinitrogen tetroxide

As for nitrogen dioxide, information about the dipole moment of dinitrogen tetroxide comes mainly from dielectric constant measurements on the equilibrium mixture. Two interpretations have been suggested. The first is that dinitrogen tetroxide has zero dipole moment and that nitrogen dioxide has a temperature-dependent one (424). The second is that dinitrogen tetroxide has a dipole moment of 0.371 D (359). Independent measurements on liquid dinitrogen tetroxide (19) show that if the Onsager formula:

$$(4\pi N\mu^2/9kT) = (M/\rho)\left\{\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2}\right\}$$

is applied to refractive index and dielectric constant data for the liquid, a value $\mu \sim 0.5$ D is found.

VI. 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 to consider the different derivatives of nitrogen dioxide and to treat dinitrogen tetroxide as a particular instance of combined nitrogen dioxide. Thus we may deal with the following sequences: (*1*) nitronium ion, NO_2^+; nitrogen dioxide, NO_2; nitrite ion, NO_2^-; hydronitrite ion, NO_2^{2-}; (*2*) derivatives of the type XNO_2; (*3*) derivatives of the type YONO.

A. THE SERIES NO_2^+, NO_2, NO_2^-, AND NO_2^{2-}

1. The nitronium ion, NO_2^+

The nitronium ion is now well known in sulfuric acid solutions of, for example, nitric acid, dinitrogen pentoxide, ethyl nitrate, and dinitrogen tetroxide (203). Numerous crystalline derivatives have also been prepared, including compounds of the anions ClO_4^-, FSO_3^-, HSO_4^-, $HS_2O_7^-$, $S_2O_7^{2-}$, $S_3O_{10}^{2-}$, NO_3^-, BF_4^-, SnF_6^{2-}, PF_6^-, AsF_6^-, SbF_6^-, and AuF_4^- (see 157, 265).

The nitronium ion has sixteen valency electrons and is thus isoelectronic with CO_2, N_3^-, BO_2^-, and numerous other linear triatomic groups. It, too, is linear and is also symmetrical. Evidence for this comes from infrared spectra (392), Raman spectra (85, 87, 152, 203, 203a, 204, 260, 380a) and x-ray crystallography (100, 125, 171). The spectroscopic measurements yield consistent values for the three fundamental frequencies (cm.$^{-1}$): $\nu_1 = 1400$; $\nu_2(2) = 537$; $\nu_3 = 2390$. Values for the N—O bond distance (Å.) lie between 1.06 (125) and 1.15 (171). In table 3, which lists these values, 1.10 ± 0.05 has been listed.

TABLE 3

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-}
Number of valency electrons (2*p*)	16	17	18	19
Interbond angle	180	134	115	110?
N—O bond length	~1.1	1.188	1.24	1.3
Vibration frequencies ($cm.^{-1}$):				
Symmetrical stretching, ν_1	1400	1361	1325	1285
Deformation, ν_2	537	770	831	885
Asymmetrical stretching, ν_3	2390	1668	1360	1200
Example of isoelectronic species	CO_2	BF_2	O_3	FO_2

2. Nitrogen dioxide, NO_2

Nitrogen dioxide has seventeen valency electrons and is unique. No isoelectronic species have been investigated, though the similar molecule PO_2, the ions FNO^+ and O_3^+, and the radical BF_2 may exist. It is not linear. Evidence for its structure comes from electron diffraction measurements (88), which give $r(N—O) = 1.20 \pm 0.02$ Å. and the apical angle = 132 ± 3°, and more recently and more precisely from infrared fine-structure measurements in the 1.4–3.4 μ region (71, 267). From these data $r(N—O) = 1.188 \pm 0.004$ Å. and the apical angle = 134° 4 ± 15′. These lead to a value of $I_1I_2I_3$ in satisfactory agreement with the calorimetric entropy (149). A recent microwave investigation (246) appears to rely on a faulty assignment.

The observed fundamental vibration frequencies (428) are listed in table 3.

3. The nitrite ion, NO_2^-

The nitrite ion has eighteen valency electrons and is isoelectronic with ozone. Like ozone, it is non-linear. This is proved by the appearance of its fundamental frequencies in both infrared (423) and Raman (224, 273) spectra. The fundamental frequencies are listed in table 3. Two recent x-ray measurements on sodium nitrite have yielded values for bond lengths and angles in approximate agreement: 1.233 Å. and 115.7° (78) and 1.247 ± 0.035 Å. and 114.2 ± 4° (398). It is interesting to note that the interbond angle in ozone is 116° and in the similar sulfur dioxide molecule is 119°. The electronic transitions in the nitrite ion have been discussed (404). Both oxygen and nitrogen are centers of electron density.

4. The hydronitrite ion, NO_2^{2-}

The hydronitrite ion, if stable, would have nineteen valency electrons and would be isoelectronic with the (hypothetical) fluorine dioxide, with chlorine dioxide, and with the ion F_2O^+. Evidence for its existence rests on the existence of the sodium salt Na_2NO_2. This has been obtained as a brilliant yellow solid from the reduction of sodium nitrite by sodium in liquid ammonia (255, 440). The ion NO_2^{2-} would be expected to have structural properties intermediate between those of ozone and fluorine monoxide; this interesting compound deserves further investigation.

5. General relations

In table 3 are listed the bond lengths, vibration frequencies, and interbond angles. This series NO_2^+, NO_2, NO_2^-, NO_2^{2-} is unique in the opportunity it affords for testing valency theories of molecular structure. The correlations are most striking (413). Increase in the number of electrons from sixteen to eighteen leads to a steady decrease in interbond angle and an increase in bond length. The force constants for bending and for asymmetrical stretching also vary markedly. The symmetrical stretching frequency is much less affected.

B. THE SERIES XNO_2 AND YONO

Nitrogen dioxide structure may also be considered in relation to combined NO_2.

1. Nitro compounds, XNO_2

In covalent compounds of the type XNO_2, where X is a univalent group, the electron distribution in the nitro group may reasonably be expected to be between the extremes of NO_2^+ and NO_2^-. In the series NO_2^+, NO_2, NO_2^- the ONO bond angle and other properties alter markedly as the number of electrons alters. Thus, in the compounds XNO_2 we might reasonably expect the ONO angle to lie between 180° and 115°. This is always so. Furthermore, on a simplified view, the ONO angle might be expected to lie between 180° and 134° when X is more electronegative than NO_2, giving the molecule some of the character of $\overset{-}{X}—\overset{+}{N}O_2$ and between 134° and 115° when the character is $\overset{+}{X}—\overset{-}{N}O_2$. Unfortunately, sufficient accurate structural data are not available to reveal these differences of bond lengths and angles. However, the same considerations apply to the force fields and to the vibration frequencies and in them this type of influence may be detected (187), the asymmetrical stretching frequency ($cm.^{-1}$) shifting from 1550 (ethyl) through 1567 (methyl), 1592 (tribromomethyl), and 1610 (trichloromethyl) to 1625 (trifluoromethyl).

The dipole moment of the $—NO_2$ group in organic derivatives is for aliphatic nitro compounds 3–3.3 D and for aromatic nitro compounds 4–4.2 D (132).

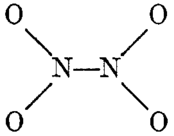
2. Covalent nitrites, YONO

In the nitrites the symmetry of NO_2 is destroyed and the two O—N links take the character of single and double bonds. Apart from some early determinations (339, 340) there are no structural data. Spectroscopic work has been done, however, on nitrous acid (207, 289, 384) and the nitrites (386). For nitrous acid 1.46 and 1.20 Å. are reported for the single and double oxygen–nitrogen bonds with an interbond ONO angle of 114° (*cis* form) and 118° (*trans* form) (385).

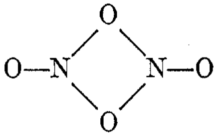
C. THE STRUCTURE OF DINITROGEN TETROXIDE

Three types of evidence are available—analogy with similar systems, chemical reactivity, and physical properties—and the best of these is physical. However, the different pieces of physical evidence are not in close agreement and evidence from chemical reactivity may be helpful. Argument by analogy with similar systems unfortunately is not easy, because not all the structures of the closely related species have been determined and those which have are quite different from one another: *viz.*, the nitric oxide dimer is a square molecule (120, 291), while solid dinitrogen pentoxide is an ionic array of NO_2^+ and NO_3^- ions (171, 392); dinitrogen trioxide is disputed (228, 290), and the analogous halogen oxides (227) have not been investigated structurally.

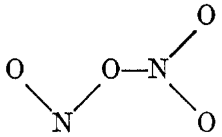
It is clear also that there are potentially three different problems, as the structure of dinitrogen tetroxide species in the solid, liquid, and gaseous states may not be the same. However, no change in Raman spectrum occurs on melting, and the infrared spectra of solid and gaseous dinitrogen tetroxide are the same (160, 262). Three structures have to be considered:



Ia, Ib



II



III

In I the molecules are linked symmetrically through an N—N bond. In Ia the molecule is planar; in Ib the two NO_2 planes are perpendicular.

In III the link is unsymmetrical; the molecule III is a true acid anhydride like gaseous dinitrogen pentoxide.

In structure II a bridge formula, similar to that successful in interpreting the boron hydrides and the nitric oxide dimer, is suggested (242).

1. Physical evidence

The existing physical evidence is as follows:

(*a*) Solid dinitrogen tetroxide has a cubic lattice. An assumed model (Ia) with N—N = 1.64 Å., N=O = 1.17 Å., and the ONO angle = 126° enabled possible x-ray reflections and *F* factors of a Fourier synthesis to be predicted. Experimental observation of x-ray patterns from a single crystal revealed 75 per cent of the reflections expected and gave *F* factors with average discrepancies of 16 per cent (70). No other models were tried.

(*b*) Infrared and Raman spectra. The spectra are very rich in lines (429) and assignment is not easy. Millen (262) states that there is a lack of coincidences in the infrared and Raman spectra. This would be produced by a molecule with a center of symmetry. Models Ia and II have a center of symmetry; models Ib and III do not.

In the Raman spectrum there is a strong line at 273 $cm.^{-1}$ which Millen assigns to the nitrogen–nitrogen stretching in model Ia (262).

(*c*) The entropy S^0 and free-energy functions $(F - H_0^0)/T$ have been measured and correlated with accurate equilibrium data (149). These values are not compatible with free internal rotation. Model II has no internal rotation. The energy barrier to rotation in model I which is necessary (47) to explain the observed entropy is 8.5–9.2 kcal. $mole^{-1}$. This is extraordinarily large in a molecule requiring only 13 kcal. to dissociate completely. Model III has two possible internal rotations and the same arguments apply against it.

(*d*) Dielectric constant measurements on the vapor (19, 358, 424) have been variously interpreted. It has been suggested (241) that in dinitrogen tetroxide there is an unusually large atomic contribution to the total polarization of the molecule and that this has obscured the interpretation.

(*e*) Theoretical calculations have been made on the basis of model Ia which lead to predicted values for bond lengths as follows: N—N, 1.57 Å.; N=O, 1.21 Å. The authors (81) consider this good agreement with x-ray studies (70).

2. Chemical evidence

In Sections VIII and IX the chemical behavior of dinitrogen tetroxide is considered more fully. The following points may be made:

a. There is ready exchange of $N^{15}O_3^-$ between tetramethylammonium nitrate dissolved in liquid dinitrogen tetroxide as the solvent, i.e., ionization of dinitrogen tetroxide yielding NO_3^- is easy (90). This is clearly true of II and III; for I, the extra assumption of easy oxygen-atom transfer is required.

b. When dinitrogen tetroxide dissolves in an ionizing medium it yields NO^+ and NO_3^-; the degree of ionization increases with the dielectric constant of the solvent.

c. With alcohols, nitrites and nitrate ion are formed; nitrates which are rapidly formed by NO_2^+ are never found.

d. With secondary amines, nitrosation again occurs.

e. With ethers and tertiary amines complexes are formed which appear to be derivatives of the solvated nitrosonium ion NO^+.

f. With metals, again nitrate ions and nitric oxide are formed.

g. With olefins and acetylenes, when addition occurs, the most recent work suggests addition of a free radical as NO_2 and not as $NO_2^+NO_2^-$.

The chemical evidence may be summarized as continually demonstrating the ease and readiness of the following reaction (28)

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

and the complete absence of the alternative heterolysis to NO_2^+ and NO_2^-, even as an intermediate stage. All three formulas are consistent with the ready homolysis to two nitrogen dioxide molecules; the facility of this reaction is the central difficulty in interpreting the chemical evidence, since at any instant pairs of nitrogen dioxide molecules are always present (even if only during the act of collision with all the configurations I to III shown). Nevertheless there is no doubt that superficially the chemistry of dinitrogen tetroxide is more readily explained by formula II or III than by formula I.

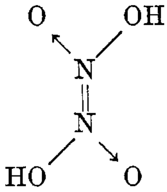
3. Analogy with similar systems and general principles

Pauling (304) pointed out that a formula of type I violated his empirical adjacent charge rule and that 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, although it has a long boron–boron distance (31b). Dinitrogen tetroxide is isoelectronic with the oxalate anion (Section XIII,E), which is also planar. Formula Ia is in accord with the physical evidence presented and is the currently accepted model.

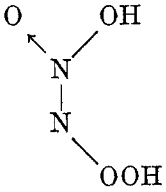
4. The ion $N_2O_4^{2-}$

When sodium hyponitrite, $Na_2N_2O_2$, is oxidized with liquid dinitrogen tetroxide compounds of the formulas $Na_2N_2O_3$ and $Na_2N_2O_4$ are formed (10). Little is yet known of their chemistry. Solid $Na_2N_2O_4$ is denser than water. It is not readily wetted. As it is wetted, nitrous oxide is slowly evolved.

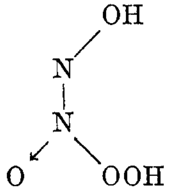
The formulas I, II, and III have been suggested for the unionized parent acid and III is considered most likely (10). No structural measurements have yet been made.



I



II



III

VII. The Reactions of Nitrogen Dioxide

A. GENERAL CONSIDERATIONS

This section deals with the chemistry of the species NO_2 and Sections VIII and IX with that of N_2O_4. Usually little difficulty arises in ascribing a particular reaction to nitrogen dioxide or dinitrogen tetroxide: thus liquid-phase reactions at low temperatures involve dinitrogen tetroxide and gas-phase reactions at high temperatures involve nitrogen dioxide. There are exceptions; in particular, reaction with unsaturated compounds. The only *kinetic* data available refer to the high-temperature gas-phase additions, where nitrogen dioxide is clearly the reactant. The other data, which come from liquid-phase studies, have been dealt with at the same time. This is supported both by the most recent work, which does suggest that they are reactions of nitrogen dioxide and not of dinitrogen tetroxide, and by practical convenience.

Nitrogen dioxide is an odd-electron molecule and a number of its reactions belong to classes typical of free radicals: for example, association reactions with other radicals, including its own dimerization, addition to unsaturated systems, and hydrogen-abstraction reactions. Other of its reactions such as photolysis, decomposition, reduction, oxidation, and its role in flames owe little to its free-radical character. A great amount of experimental work has been based on the use of nitrogen dioxide as a sensitizer of chemical reactions and explosive ignitions. For this reason these are treated, but in outline only, as they afford little information about nitrogen dioxide itself.

Throughout, attention is focussed on the individual steps and similar individual reactions are classified together. Although precise kinetic data are not always available for every example, this approach indicates where new data are particularly desirable and permits comparative estimates to be made in the meantime. Superficially this approach may appear to be made at the expense of the complete description of any given complex reaction but the conventional approach, if required, is to be found in most papers and reviews.

Two particularly useful summaries may be mentioned: Johnston's review (208) of the reactions related to the decomposition of N_2O_5, which is altered but little by newer data, and Bachmann, Hass, and Hewett's summary of hydrocarbon nitration (35).

B. THE ASSOCIATION OF NO_2 WITH OTHER RADICALS

When free radicals collide they may either separate without forming a stable chemical bond or they may combine. Internal rotations and vibrations may serve as a temporary store for the energy of recombination until it can be passed on in collisions, and it is possible for recombination to have second-order kinetics though at low pressures it will be third order.

When nitrogen dioxide is one of the radicals, two distinct associations are possible (163): nitro compound formation or nitrite formation. When association yields a nitrite XONO through O—X bond formation, the O—N bond strength is low enough for its fission to follow rapidly, yielding the alkoxy radical and nitric oxide. Thus the alternatives are:

$$X + NO_2 \rightarrow XNO_2 \qquad \text{Association}$$

$$X + NO_2 \rightarrow XO + NO \qquad \text{Metathesis}$$

The observed rate of metathesis is strongly influenced by the strength of the oxygen–nitrogen bond and such reactions form a quite separate class (see Section VII,E). For the association reaction detailed kinetic data are not always available, for many of these reactions have been observed only in complex systems and not studied in isolation. Frequently, however, the reverse reactions

$$XNO_2 \rightarrow X + NO_2$$

have been followed and sufficient information about them gathered to increase the population of this class of reaction considerably.

1. Association with atoms

The reaction

$$H + NO_2 \rightarrow \text{"}HNO_2\text{"}$$

was postulated as a step occurring in the nitrogen dioxide-sensitized reaction between hydrogen and oxygen (236). If "HNO_2" is nitrous acid, reaction is exothermic by some 80 kcal. and association is probably rapidly followed by formation of HO and NO. When fluorine reacts with nitrogen dioxide, atoms of fluorine associate rapidly with NO_2 after a slow initial reaction:

$$F_2 + NO_2 \rightarrow F + FNO_2$$

$$F + NO_2 + M \rightarrow FNO_2 + M$$

The association reaction is third order at the low pressures (∼2 mm.) studied (32, 306).

Chlorine atoms and nitrogen dioxide behave similarly; the second-order unimolecular decomposition of nitryl chloride proceeds by the exact reverse of the steps above (96) and the association

$$Cl + NO_2 + M \rightarrow ClNO_2 + M \qquad \Delta H = -29{,}500 \text{ kcal.}$$

is third order at pressures of a few millimeters. At 500°K. K_c (mole cc.$^{-1}$) = $(Cl)(NO_2)/(NO_2Cl) = 9.6 \times 10^{-12}$.

2. Association with radicals

Association to nitro compounds and to nitrites has been observed with many radicals. With hydroxyl radicals, both types have been observed in reverse and association to nitric acid has also been detected (210, 211).

$$NO_2 + HO \rightleftharpoons HNO_3$$

At pressures below 1 atm. the dissociation of nitric acid becomes second order; hence association to nitric acid at low pressures requires a third body. The experimental activation energy of 40 kcal. for the dissociation of nitric acid is lower than the HO—NO_2 bond dissociation energy of 52 kcal.

Hydroxyl radicals may also associate to yield pernitrous acid, HOONO, since the pyrolysis of pernitrous acid (174) has been demonstrated to yield HO + NO_2 (175, 195, 225). Nitric oxide and nitrogen trioxide, no less than nitrogen dioxide, are radicals and all may associate with one another. The dimerization of nitrogen dioxide has been described in Section III. At atmospheric pressure it is second order; by 0.5 atm. it is third order with zero or negative activation energy. The second-order velocity constant for association corresponds to a steric factor of 5×10^{-3} if the molecular diameter of nitrogen dioxide is set at 4.6 Å.

Association with nitric oxide yields dinitrogen trioxide. If 100 volumes of each are mixed at atmospheric pressure the composition changes have been given as (2, 116):

	N_2O_4	NO_2	NO	N_2O_3	Total
Before mixing...........	68	32	100	—	100
After mixing............	62	38	94	6	100

corresponding to equilibrium constants:

$$NO_2 + NO = N_2O_3$$

$$K_p \text{ (atm.}^{-1}) = -2.105 + 45.63\, C^0_{N_2O_3}$$

$$\Delta G^0 = +441 \text{ cal.}$$

$$\Delta S^0 = -30 \text{ cal. deg.}^{-1}$$

Experiments with isotopic nitrogen show that the activation energy of oxygen exchange is 10.5 kcal. If the formula of dinitrogen trioxide is ONONO, then this is close to the enthalpy of dissociation. It has been suggested, however, that dinitrogen trioxide is $ON \cdot NO_2$ (290).

With nitrate radicals ($\bullet NO_3$) association yields dinitrogen pentoxide. Both this association and the reverse reaction have received much attention at the hands of the interpreters of the decomposition of dinitrogen pentoxide and allied reactions. The isotope-exchange reaction (285) between $N_2^{15}O_4$ and N_2O_5 is rapid in the gas phase and solution; it occurs by association and oxygen-atom transfer. For the association reaction:

$$NO_2 + NO_3 \xrightarrow{k_2} N_2O_5 \qquad \Delta H \sim -18 \text{ to } -22 \text{ kcal.}$$

and $k_2 = 4 \times 10^9$ liter/mole sec., corresponding to $A = 2 \times 10^{10}$ and $E = 1 \pm 4$ kcal.

Association of nitrogen dioxide with oxygen molecules has been postulated (285) to explain the exchange reaction between O_2^{16} and O_2^{18} in the presence of dinitrogen pentoxide. The product is written as a pernitrate radical, NO_4.

Of the association with alkyl radicals, numerous examples are known; it is the actual step by which nitroparaffins are formed in the vapor-phase nitration of hydrocarbons (35, 36, 146a, 178, 184, 197, 342, 436). Association is also encountered in other systems: e.g., the pyrolysis and photolysis of alkyl nitrates (161, 229) and the reaction between nitrogen dioxide and tetraethyllead (72, 251) or acetaldehyde (249). In reverse, it has been postulated as the initial step in nitroparaffin pyrolysis (99, 142, 170). Actual experimental evidence is available for association to nitro compounds for the following alkyl radicals: methyl (35, 36, 72, 161, 178, 184, 197, 229, 342, 436), ethyl (35, 36, 184, 197); *n*- and *sec*-propyl (36); *n*-, *sec*-, iso-, and *tert*-butyl (36, 342); *n*- and *sec*-amyl (436).

No kinetic data are available, though they might be expected to have much in common with, for example, the analogous reactions:

	ΔH	*Steric factor*
$CH_3 + CH_3 \rightarrow C_2H_6$	-86 kcal.	$P = 1$
$NO_2 + NO_2 \rightarrow N_2O_4$	-13 kcal.	$P = 5 \times 10^{-3}$
$CH_3 + NO_2 \rightarrow CH_3NO_2$	-57 kcal.	$P = ?$

From a recent study of these systems (163) several generalizations emerge: (*1*) Association to nitro compound is easy and stabilization is easy. (*2*) Association to nitrite is easy but stabilization is difficult because to prevent subsequent O—N bond fission energy equivalent to 20 kcal. mole^{-1} has to be dissipated. Because of this nitrites are *not* formed directly in the gas phase, though they may be formed in solution. (*3*) Low temperatures and high pressures of an inert gas favor association.

The only example of direct nitrite formation by radical–radical association occurs in solution between nitrogen dioxide and triphenylmethyl radicals when trityl nitrite is formed (353), as well as the nitro compound.

The perfluoroalkyl radicals C_nF_{2n+1} behave in the same way (188). They form nitro compounds readily, and no nitrites have been isolated from the system. It is also likely that trichloromethyl radicals associate to form chloropicrin; the decomposition products of chloropicrin can be readily explained (163) by postulating dissociation as the initial step.

The association reaction with alkoxy radicals to form an alkyl nitrate plays an important part in nitrate pyrolyses, as was first suggested by Phillips (308).

$$RO + NO_2 \rightarrow RONO_2$$

Thus, added nitrogen dioxide has been found to retard the decomposition of nitrates and to lead to the formation of ethyl nitrate in the pyrolysis of ethyl nitrite (313). The pyrolysis of a nitrate (which principally yields information about the reverse of association) is a first-order reaction down to a few centimeters pressure and thus the corresponding associations do not show the need for a third body. All the associations (equation above) liberate some 35–40 kcal. mole^{-1}.

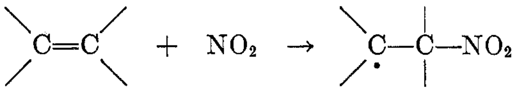
Further details of these associations may be found in descriptions of the pyrolyses of, for example, methyl nitrate (29, 162, 168, 169), ethyl nitrate (3, 162, 168, 169, 229, 308), *n*-propyl nitrate (166, 229), *sec*-propyl nitrate (166), and *tert*-butyl nitrate (229).

C. ADDITION OF NITROGEN DIOXIDE TO UNSATURATED COMPOUNDS

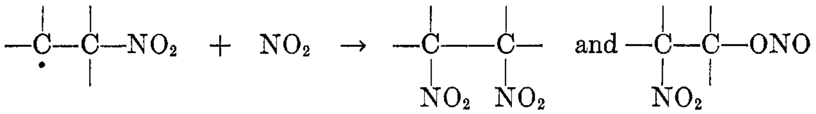
The addition reactions of dinitrogen tetroxide have been known for many years; work up to 1944 is described by Riebsomer (336). Addition has been interpreted in various ways, and the last word has not been said. The most recent evidence (348, 349) favors free-radical attack by NO_2 species. The older view was (38, 232, 233, 234, 235) expressed in terms of complete or incipient heterolysis to NO_2^+ and NO_2^-. Little kinetic evidence is available, although useful comparative studies have been made on nitryl chloride.

1. Addition to olefins

Reactions have been studied in the gaseous and liquid phases between pure reactants and in solution (232, 336). Solvents which have been used are diethyl ether, ethyl acetate, and dioxane. Reaction in solution is carried out at low temperatures by passing a stream of gaseous olefin through the solution of nitrogen dioxide at −10° to −25°C.; liquid olefins are added dropwise. The primary products of reaction appear always to be dinitro compounds and nitro-nitrites, often in nearly equal proportions (232). Secondary reactions give rise to other species; nitro olefins, nitro nitrates, and nitro alcohols have all been found. In the gas phase at elevated temperatures addition is followed by complete oxidation. In the liquid phase oxidation is diminished by the presence of the solvent (232).



(7a)



$$-\underset{\bullet}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-NO_2 + NO_2 \rightarrow -\underset{NO_2}{\overset{|}{C}}-\underset{NO_2}{\overset{|}{C}}- \text{ and } -\underset{NO_2}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-ONO \qquad (7b)$$

In solution, ethylene reacts slowly at atmospheric pressure, giving 1,2-dinitroethane and 2-nitroethyl nitrite (which in turn yields the nitrate). Propylene and the butylenes react rapidly, giving the 1,2-dinitro compounds and β-nitroisopropyl nitrate and nitro-*tert*-butyl nitrate. Addition of the first NO_2 seems always to form the nitro compounds, the second NO_2 may yield either nitro compound or nitrite.

Kinetic studies in the gas phase have been made of the reaction of nitrogen dioxide with ethylene and propylene (97, 98). Reaction was followed photometrically, and simultaneous measurements of pressure were made. Analyses of the final gaseous products, but not of the intermediate stages, were made. The results for ethylene between 160° and 280°C. gave a kinetic expression which could be fitted to the equation

$$-d[NO_2]/dt = k[NO_2]^2[C_2H_4]$$

although the exponents differed slightly from whole numbers and k was not the same over the whole temperature range. From 160° to 220°C. $k = 10^{8.5} \exp(-12{,}500/RT)$; from 220° to 280°C. $k = 10^{10.9} \exp(-18{,}000/RT)$. It was thought that addition was the primary step and that simultaneous reactions with different activation energies were proceeding. The products of addition are dinitroethane and 2-nitroethyl nitrite. At 150°C. Levy (231) found that very little dinitroethane remained, but that nitroethylene and nitroethanol were among the main products. At these temperatures the concentration of dinitrogen tetroxide is far too small to account for the observed rate (despite the factor $[NO_2]^2$) and the rate equation has been attributed to reaction 7a being fast and 7b rate-controlling (393).

Similar behavior is shown by propylene (98); the reaction is about three times faster than with ethylene, and again follows the kinetic equation

$$-d[NO_2]/dt = k[NO_2]^2[C_3H_6]$$

with k (liter^2 mole^{-2} sec.$^{-1}$) $= 10^{9.7} \exp(-13{,}600/RT)$ between 160° and 260°C. Below 160°C. the activation energy is lower. No analyses are recorded.

The products of addition to unsymmetrically substituted olefins offer an opportunity of deciding the mechanism. Methyl acrylate and other acrylic esters have been studied (348, 349). It is found that addition of NO_2 at the terminal position occurs exclusively by C—N bond formation The second NO_2 is added as either C—ONO or C—NO_2. The same type of addition takes place irrespective of the electronic demands of the group attached to the unsaturated system. This evidence also argues against addition of N_2O_4 as an electrophilic reagent.

Some reactions of fluorinated olefins and nitrogen dioxide have been reported

(30, 54, 91, 186). Thus from $CF_2{=}CF_2$, $CF_2{=}CFCl$, and $CF_2{=}CCl_2$ dinitro compounds have been isolated (186).

Work on the addition to olefins of nitrosyl and nitryl chlorides (44, 69, 317, 336, 348, 364, 380, 404a) is also of value in interpreting the behavior of nitrogen dioxide.

2. Addition to acetylenic compounds

Kinetic measurements have recently been made on the gas-phase reaction between acetylene and nitrogen dioxide between 170° and 220°C. (393). Reaction is second order, with k (liter mole^{-1} sec.^{-1}) given by $10^{7.1}\exp(-15{,}000/RT)$. It is suggested that reaction involves addition of NO_2 in two steps, forming the dinitrite derivative; the kinetics require addition of the first NO_2 group to control the rate. The glyoxal produced in this reaction is said to be formed from the ethylene dinitrite. At low temperatures the reaction between acetylene and dinitrogen tetroxide takes place very slowly (77).

The addition reaction with tolane ($C_6H_5C{\equiv}CC_6H_5$) in ether at 0–25°C. has been examined (77). The products of reaction were *cis*- and *trans*-dinitrostilbene and 5-nitro-2-phenylisatogen. A free-radical mechanism is proposed to account for the *cis* addition; the formation of the isatogen derivative may be explained on this basis.

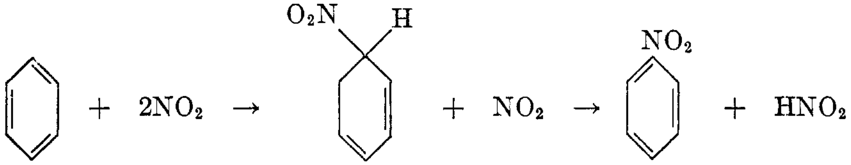
The products of the reaction of numerous acetylenic systems have been tabulated by Riebsomer (336). (See also reference 354a.)

The addition of nitryl chloride to simple acetylenic systems has also been studied (69); $ClC{\equiv}CCl$ gives $Cl_2C{=}CClNO_2$.

3. Addition to aromatic systems

Many references to the reaction between aromatic compounds and nitrogen dioxide are listed by Riebsomer (336). Mixtures of aromatic hydrocarbons react in the gas phase with nitrogen dioxide to give nitration products. Reaction may be brought about by heating to 80°C. in sealed tubes, by heating to higher temperatures in diluted gas mixtures, by the action of light (λ 4000–7000 Å.) at 55–60°C., or by a glow discharge in a Siemens tube.

A mechanism proposed recently by Titov (401) for the high-temperature reaction is essentially addition of NO_2 followed by abstraction of a hydrogen atom by further NO_2:

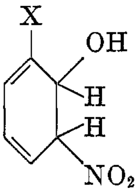


Subsequent stages are given a more complex interpretation (401).

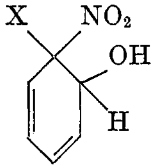
The interaction of nitrogen dioxide and aromatic compounds forms a part of the reaction between pernitrous acid (HOONO) and aromatic compounds (174, 175, 195, 225). Pernitrous acid both hydroxylates and nitrates benzene; it undergoes homolytic fission to give hydroxyl radicals and nitrogen dioxide:

$$HOONO \rightarrow HO + NO_2$$

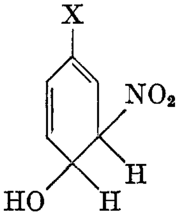
(In agreement with this suggestion, pernitrous acid is found to initiate the polymerization of methyl acrylate.) The mechanism proposed is free-radical addition of hydroxyl to give an aryl radical, which then associates with NO_2. The type of product is illustrated in substituted benzenes, C_6H_5X, by A, B, and C:



A

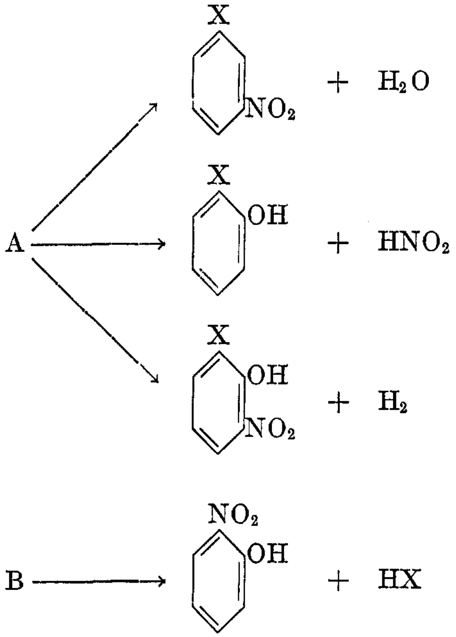


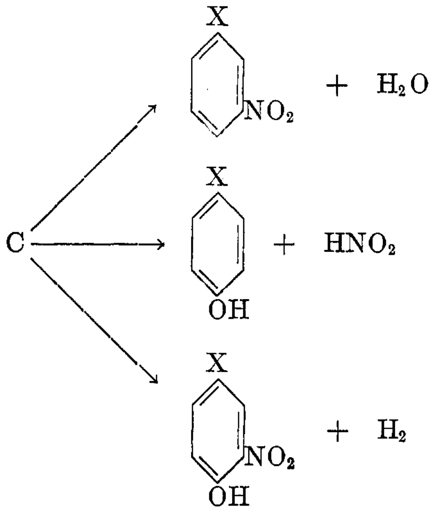
B



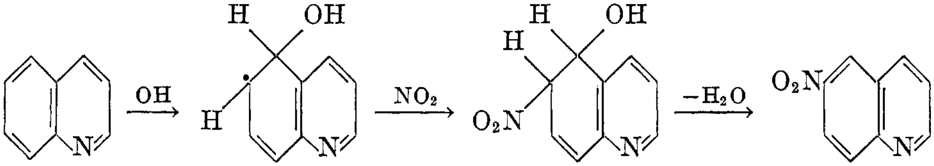
C

These addition compounds break down by elimination of H_2O, HONO, and H_2; for example, some of the reactions are as follows:





It is found that hydroxylation nearly always occurs in the ortho or para position in substituted aromatics and nitration exclusively in the meta position. Alternative schemes, e.g., involving ionic species such as NO_2^+ and NO^+, have been excluded by the work of Robinson and coworkers (174, 175, 195). A similar mechanism has been suggested (225) for the formation from pernitrous acid and quinoline in aqueous acetic acid of 6- and 7-nitroquinoline:



Some of the reaction products obtained with pernitrous acid and benzene are given in table 4.

TABLE 4

Products of reaction of pernitrous acid and some aromatic compounds (175)

Material	Non-phenolic Products		Phenolic Products	
	Major	Minor	Major	Minor
C_6H_6	$C_6H_5NO_2$	$C_6H_5C_6H_5$ p-$C_6H_4(NO_2)_2$	o-$O_2NC_6H_4OH$	C_6H_5OH p-$C_6H_4(NO_2)OH$ 1,3,4-$C_6H_3(C_6H_5)(NO_2)OH$ 1,2,4-$C_6H_3OH(NO_2)_2$
$C_6H_5CH_3$	$CH_3C_6H_4NO_2$ C_6H_5CHO	—	1,2,6- and 1,4,2-$C_6H_3(OH)(CH_3)(NO_2)$	
$C_6H_5NO_2$	m-$C_6H_4(NO_2)_2$	o- and p-$C_6H_4(NO_2)_2$	o-, m-, and p-$C_6H_4(NO_2)OH$	
C_6H_5Cl	m-$C_6H_4ClNO_2$	p-$C_6H_4ClNO_2$	o-C_6H_4ClOH 2,4,1-$C_6H_3(NO_2)Cl(OH)$	

D. HYDROGEN-ABSTRACTION REACTIONS

To its free-radical character nitrogen dioxide owes another characteristic mode of reaction—abstraction of hydrogen from an organic molecule to leave an alkyl radical.

$$RH + NO_2 \rightarrow R\cdot + HONO \tag{1}$$

Obviously such a step is easier the weaker the original R—H bond. Thus this hydrogen-abstraction reaction initiates gas-phase nitration and oxidation of hydrocarbons, and it is found that attack is easiest on tertiary C—H bonds and hardest on primary. In the reactions of aldehydes with nitrogen dioxide the aldehydic C—H bond of RCHO is considerably weaker than in hydrocarbons; in fact, oxidation of an aldehyde is observed at temperatures 200° lower than the oxidation of a hydrocarbon. Conversely, olefinic and acetylenic C—H bonds are stronger, and addition takes precedence over hydrogen abstraction.

The initial step (equation 1) is rapidly succeeded by secondary reactions of the alkyl radical. Prominent among these are nitration (equation 2) and oxidation (equation 3).

$$R + NO_2 \rightarrow RNO_2 \tag{2}$$

$$R + NO_2 \rightarrow RO + NO \tag{3}$$

All the overall reactions are complex. Their extents are dependent on temperature, pressure, and the presence of catalysts and involve many different types of individual steps, so that detailed kinetic information is often incomplete. However, initial abstraction of a hydrogen atom is able to account satisfactorily for the observed properties in the examples following. The subsequent steps such as radical-radical association and metatheses are dealt with elsewhere in this review. Here overall reactions are described only in outline, attention being focussed on the initial step.

1. Hydrogen abstraction from hydrocarbons: the nitration of paraffins

The lowest members are the least reactive members of the series of normal paraffins. With propane and higher hydrocarbons reaction occurs more readily and mixtures of nitro compounds are formed (146a, 183a, 232a, 407a). At low temperatures the ease of abstraction (342) increases from primary through secondary to tertiary hydrogen. At intermediate temperatures, lower nitroparaffins are formed by degradation of higher hydrocarbons; for this reason nitromethane is manufactured from propane and not directly from methane (183a).

At still higher temperatures, three visually distinct modes of reaction are possible: (*1*) slow reaction, (*2*) emission of blue luminescence, (*3*) violent explosion (436).

The homogeneous gas-phase reaction between methane and nitrogen dioxide occurs only at relatively high temperatures (436). There is no appreciable reaction below 300°C. (182). Between 350° and 450°C. nitromethane is formed in a second-order reaction (178). For this reaction:

$$d[CH_3NO_2]/dt = k[NO_2][CH_4]$$

$$k\ (\text{liter mole}^{-1}\ \text{sec.}^{-1}) = 10^6 \exp(-21{,}000/RT)$$

At temperatures above 430°C. formaldehyde predominates among the products (144, 370). Above 450°C. explosion is possible (436); the final products are water, carbon monoxide, carbon dioxide, and nitric oxide. The course of the reaction is probably:

$$CH_4 + NO_2 \rightarrow CH_3 + HONO$$

$$HONO \rightarrow HO + NO$$

$$CH_4 + HO \rightarrow CH_3 + H_2O$$

$$CH_3 + NO_2 \rightarrow CH_3NO_2$$

$$CH_3 + NO_2 \rightarrow CH_3O + NO$$

$$CH_3O + NO_2 \rightarrow CH_2O + HONO$$

$$CH_3O + OH \rightarrow CH_2O + H_2O$$

Propane reacts between 250° and 360°C., giving a mixture of products among which 2-nitropropane predominates, especially in the early stages (118). The principal products are 2-nitropropane, 1-nitropropane, nitromethane, and nitroethane; in addition, small amounts of 2,2-dinitropropane, acetone, carbon monoxide, and nitric oxide are formed. The range of composition may be illustrated by the following extreme values of products formed at 423°C.: nitromethane, 9–49 per cent; nitroethane, 6–36 per cent; 1-nitropropane, 2–35 per cent; 2-nitropropane, 5–45 per cent. The reaction is affected by homogeneous catalysts such as chlorine and oxygen by virtue of their own ability to generate alkyl radicals, by reactant ratios, and by reactor temperature. Increased temperature favors nitroethane at the expense of 2-nitropropane. Common solid catalysts (Fe_2O_3, B_2O_3) and salt-like catalysts have no effect (33, 34, 35, 118, 184).

The reaction mechanism may be summarized:

$$CH_3CH_2CH_3 + X\ (NO_2, Cl, O_2) \rightarrow \begin{cases} (CH_3)_2CH\cdot \rightarrow \text{2-nitropropane} \\ CH_3CH_2CH_2\cdot \rightarrow \text{1-nitropropane} \end{cases}$$

$$(CH_3)_2CH\cdot + NO_2 \rightarrow (CH_3)_2CHO\cdot + NO$$

$$\rightarrow CH_3CHO + CH_3\cdot \rightarrow \text{nitromethane}$$

$$CH_3CH_2CH_2\cdot \rightarrow CH_3CH_2CH_2O \rightarrow CH_2O + C_2H_5\cdot \rightarrow \text{nitroethane}$$

$$(CH_3)_2CHNO_2 \rightarrow \text{2-nitropropane}$$

$$(CH_3)_2CHO\cdot + X\ (NO_2, Cl, O_2, R) \rightarrow \text{acetone}$$

Less detailed data are available for the higher hydrocarbons. The nitration of *n*-butane by nitric acid (34, 184) is initiated by hydrogen abstraction, but the agent is probably HO and not NO_2. Isobutane yields much more of the tertiary isomer, $(CH_3)_3CNO_2$ (342). Pentane has been studied at 220–300°C. (346), the consumption of nitrogen dioxide being followed photometrically. Nitric oxide is the most abundant gaseous constituent. Secondary nitroparaffins predominate, though small amounts of nitrites and primary nitroparaffins are formed. For hydrocarbons above C_5 Riebsomer's review may be consulted; relatively little recent work has been published.

The results of studies on the vapor-phase nitration of hydrocarbons by nitrogen dioxide may be summarized as follows: (*1*) The initial step is hydrogen abstraction. This occurs most easily from a tertiary or a secondary carbon atom; in the normal series the rate of reaction increases from methane to pentane. (*2*) Substances which themselves abstract hydrogen, e.g., oxygen and chlorine, catalyze the reaction. (*3*) Side reactions subsequent to the initial step increase in importance with increasing temperature, forming lower radicals and nitroparaffins.

2. Hydrogen abstraction from aldehydes

The success of hydrogen abstraction in explaining the reaction of nitrogen dioxide with paraffins encourages its application to the reaction of nitrogen dioxide with aldehydes. In paraffins as the C—H bond energy diminishes in the series primary, secondary, tertiary, so attack by nitrogen dioxide is facilitated. The aldehydic C—H link is still weaker and the same mechanism gives a satisfactory explanation:

$$RCHO + NO_2 \rightarrow R\underset{\bullet}{C}O + HONO$$

Differences in subsequent behavior are due to differences in the properties of R• and RCO•. There is no *stable* $RCO \cdot NO_2$ corresponding to a nitro compound and oxidation is favored.

$$RCO + NO_2 \rightarrow RCO_2 + NO$$

$$RCO_2 \rightarrow R + CO_2$$

$$R + NO_2 \rightarrow RNO_2 \text{ etc., as before}$$

Only the simplest aldehydes have as yet been studied quantitatively. The slow gas-phase reaction between formaldehyde and nitrogen dioxide has been studied manometrically in a mixture containing $HCHO + 2NO_2$ (314) in the temperature range 118–184°C. Reaction is homogeneous and at 150°C. obeys the relation

$$dp/dt = k[NO_2][HCHO]$$

$$\text{Below 160°C. } k \text{ (liter mole}^{-1}\text{ sec.}^{-1}) = 10^{7.1} \exp(-15{,}100/RT)$$

$$\text{Above 160°C. } k \text{ (liter mole}^{-1}\text{ sec.}^{-1}) = 10^{9} \exp(-19{,}000/RT)$$

The products of reaction are nitric oxide, carbon monoxide, carbon dioxide, and water; hydrogen is not found. Traces of nitrogen and nitrous oxide may be present. The relative proportions of carbon monoxide and carbon dioxide at a given temperature are independent of the relative concentrations of formaldehyde and nitrogen dioxide. Reaction has been interpreted in terms of hydrogen abstraction (394) according to the following scheme:

$$\begin{aligned} \mathrm{HCHO + NO_2} &\rightarrow \mathrm{CHO + HONO} \\ \mathrm{CHO + NO_2} &\rightarrow \mathrm{HCO_2 + NO} \\ \mathrm{CHO + NO_2} &\rightarrow \mathrm{CO + HONO} \\ \mathrm{HCO_2 + NO_2} &\rightarrow \mathrm{CO_2 + HONO} \\ \mathrm{2HNO_2} &\rightarrow \mathrm{H_2O + NO + NO_2} \end{aligned}$$

giving

$$\mathrm{d}p/\mathrm{d}t = k[\mathrm{HCHO}][\mathrm{NO_2}]$$

and

$$\frac{\mathrm{d[CO]}}{\mathrm{d[CO_2]}} = \text{constant}$$

in agreement with experiment.

Acetaldehyde also reacts readily with nitrogen dioxide in the temperature range 100–150°C. (72, 249). The reaction has been followed by optical absorption (249) and by infrared analyses of formaldehyde and nitrogen dioxide (72). Both sets of experiments lead to the expression:

$$\text{Rate of reaction} = k[\mathrm{CH_3CHO}][\mathrm{NO_2}]$$

The more detailed study gives

$$k\ (\text{liter mole}^{-1}\ \text{sec.}^{-1}) = 10^7 \exp(-13{,}500/RT)$$

Three moles of nitrogen dioxide per molecule of acetaldehyde are required. The principal products are water, nitric oxide, and carbon dioxide; acetic acid and carbon monoxide are not formed in significant amounts, but methyl nitrate, nitromethane and, in the later stages of reaction, methyl nitrite have all been detected. The mechanism is:

$$\left.\begin{array}{lrl} 1. & \mathrm{CH_3CHO + NO_2} & \rightarrow \mathrm{CH_3CO + HONO} \\ 2. & \mathrm{2HONO} & \rightarrow \mathrm{H_2O + NO + NO_2} \\ 3. & \mathrm{CH_3CO + NO_2} & \rightarrow \mathrm{CH_3COO + NO} \\ 4. & \mathrm{CH_3COO} & \rightarrow \mathrm{CH_3\cdot + CO_2} \\ 5. & \mathrm{CH_3 + NO_2} & \rightarrow \mathrm{CH_3O + NO} \end{array}\right\}\text{Principal reactions}$$

$$\left.\begin{array}{lrl} 6. & \mathrm{CH_3 + NO_2} & \rightarrow \mathrm{CH_3NO_2} \\ 7. & \mathrm{CH_3O + NO_2} & \rightarrow \mathrm{CH_3ONO_2} \end{array}\right\}\text{End products from early stages}$$

$$\begin{array}{lrl} 8. & \mathrm{CH_3O + NO} & \rightarrow \mathrm{CH_3ONO} \end{array}\quad\text{End product from late stages}$$

The acidic residue reported by McDowell and Thomas (249) may have arisen from hydrolyzed nitrite; they reported a slightly different velocity constant, $k = 10^{9.859} \exp(-16{,}000/RT)$. Glyoxal oxidation is also considered to be initiated by hydrogen abstraction (394). The gas-phase reaction between 160° and 210°C. is homogeneous and second order, the value of k (liter mole^{-1} sec.$^{-1}$) being given by:

$$k = 10^{8.9} \exp(-19{,}800/RT)$$

The products of reaction are nitric oxide, water, carbon monoxide, carbon dioxide, and glyoxylic acid; the relative amounts of carbon monoxide and carbon dioxide vary with the initial concentrations of reactants. The scheme proposed is

$$\begin{gathered}
(CHO)_2 + NO_2 \xrightarrow{k} COCHO + HONO \\
2HONO \rightarrow H_2O + NO + NO_2 \\
COCHO + NO_2 \rightarrow CO_2CHO + NO \\
COCHO + NO_2 \rightarrow COCO + HONO \rightarrow 2CO \\
CO_2CHO + NO_2 \rightarrow CO_2CO + HONO \rightarrow CO + CO_2 \\
CO_2CHO + (CHO)_2 \rightarrow COOHCHO + COCHO
\end{gathered}$$

3. Hydrogen abstraction from ethers, alcohols, ketones, and acids

Dimethyl, diethyl, dipropyl (*n*- and *sec*-), di-*n*-butyl, and methyl *n*-butyl ethers have been nitrated in the vapor phase at 400°C. (185). Nitro ethers are formed and, in addition, all the possible nitroalkanes are produced after fission of the carbon–oxygen and carbon–carbon bonds. The α-hydrogen atoms are not attacked, though all other hydrogen atoms can be replaced. The results are summarized in table 5.

Under these conditions the alcohols ethanol, 1-propanol, 1-butanol, and 2-methyl-1-propanol do *not* yield nitroalcohols but form lower nitroalkanes after

TABLE 5

Products of reaction between ethers, alcohols, ketones, and nitrogen dioxide

Compound Nitrated	Products Identified
Dimethyl ether	Nitromethane
Diethyl ether	Nitromethane, nitroethane, β-nitroethyl ether
Diisopropyl ether	Nitromethane, 2-nitropropane, β-nitroisopropyl ether
Di-*n*-propyl ether	Nitromethane, nitroethane, 1-nitropropane
Methyl *tert*-butyl ether	Nitromethane
Di-*n*-butyl ether	Nitromethane, nitroethane, 1-nitropropane, 1-nitrobutane
Ethanol	Nitromethane
1-Propanol	Nitromethane, nitroethane
1-Butanol	Nitromethane, nitroethane, 1-nitropropane
2-Methyl-1-propanol	Nitromethane, nitroethane, 2-methyl-2-nitro-1-propanol
Acetone	Nitromethane
Diisopropyl ketone	Nitromethane, 2-nitropropane, 2,4-dimethyl-2-nitro-3-pentanone, 2,4-dimethyl-1-nitro-3-pentanone
Di-*n*-propyl ketone	Nitromethane, nitroethane, 1-nitropropane, 1-nitro-4-heptanone, 1,1-dinitropropane

fission of carbon–carbon bonds (185). It is possible that nitrite formation is the initial step.

Acetone and the two symmetrical dipropyl ketones give mononitroketones and nitroalkanes, though cyclohexanone produces only adipic acid (185).

Propionic acid yields β-nitropropionic acid (185). Formic acid reacts at a measurable rate at 200°C., the products being quantitatively carbon dioxide and nitric oxide (311).

4. Hydrogen abstraction from other organic compounds

Nitromethane is attacked by nitrogen dioxide in the temperature range 400–500°C.; the principal products are formaldehyde and nitric oxide (178). The reaction has been written:

$$CH_3NO_2 + NO_2 \rightarrow CH_2NO_2 + HONO$$

$$CH_2NO_2 \rightarrow HCHO + NO$$

although there is as yet little evidence in support of this.

E. METATHETICAL REACTIONS

1. Oxidation by nitrogen dioxide

$$NO_2 + X \rightarrow NO + XO$$

In this class of reaction an oxygen atom is transferred from the nitrogen dioxide molecule. The geometry of the intermediate state $X\cdots O\cdots NO$ must have much in common with a nitrite, and thus factors which influence association reactions may also influence metatheses. However, the step following association will play a part at least equally important. Oxidation by nitrogen dioxide cannot be expected to belong to the same class of reactions as association and addition (*cf.* 415). Many oxidations by nitrogen dioxide are known. The examples considered here may all be written:

$$NO_2 + X \rightarrow NO + XO$$

where X may be an atom (H, N, O, Na), a radical (C_nH_{2n+1}, C_nF_{2n+1}, CH_3CO, CCl_3), an odd-electron molecule (NO, NO_2, O_2, NO_3), or a normal molecule (CO, SO_2, NOCl). When detailed kinetic information is lacking about these reactions, it may be supplemented by thermodynamic data and by kinetic data for the reverse reaction. The principle of detailed balancing then enables valid inferences to be drawn about the forward reaction.

(a) Oxidation of atoms by nitrogen dioxide

Additions of nitrogen dioxide have a pronounced effect on the hydrogen–oxygen reaction, especially near the explosion limits (Section VII). Among others, the reaction

$$H + NO_2 \rightarrow HO + NO \qquad \Delta H = -30 \text{ kcal. mole}^{-1}$$

has been postulated (31); the species HNO_2 may be an intermediate (236).

Nitrogen atoms react to form two molecules of nitric oxide:

$$N + NO_2 \rightarrow 2NO \qquad \Delta H = -78 \text{ kcal.}$$

This reaction occurs when nitrogen dioxide is used to quench the strong afterglow of nitrogen from air streaming through an electrodeless discharge; the same reaction occurs during the neutron irradiation of nitrogen dioxide (183). If more nitrogen dioxide or nitric oxide is added, the oxygen afterglow, due to the combination of oxygen atoms and nitric oxide, appears.

$$NO + N \rightarrow N_2 + O \qquad \Delta H = -75 \text{ kcal.}$$

$$O + NO \rightarrow NO_2 \qquad \Delta H = -71 \text{ kcal.}$$

Still further additions of nitrogen dioxide (but not nitric oxide) quench the oxygen afterglow

$$NO_2 + O \rightarrow NO + O_2 \qquad \Delta H = -45 \text{ kcal.}$$

by reacting with oxygen atoms. This reaction of nitrogen dioxide with oxygen atoms also occurs in its photolysis. The activation energy is close to 4 kcal. mole^{-1}; at room temperature one in every 10^5 collisions leads to reaction (193, 361, 375).

The reaction between sodium atoms and nitrogen dioxide has been investigated by the Polanyi diffusion flame technique (42). Reaction was ascribed to:

$$Na + NO_2 \rightarrow NaO + NO \qquad \Delta H \sim 0$$

and a second-order velocity constant (liter mole^{-1} sec.$^{-1}$) of 6 to 1.5×10^{10} with $E \sim 2.4$ kcal. inferred.

(b) Oxidation of free radicals by nitrogen dioxide

As described in Section VII,B, although free radicals may associate with nitrogen dioxide to yield either a nitrite type or a nitro type of product, only the nitro type is stable and the nitrite decomposes by oxygen–nitrogen bond fission to produce the overall result:

$$R + NO_2 \rightarrow RO + NO$$

These reactions have been discussed by Gray (163). When R is an alkyl radical the process is exothermic by some 20 kcal. The species RO is itself very reactive (164) and splits out most readily the largest alkyl group, leaving a carbonyl compound. The alkyl radical continues to react in the same way. This oxidation of alkyl radicals plays an important role in the nitration of paraffins when alkoxy formation and fission is the source of the lower nitroparaffins formed (Section VII,D).

Useful references to some of these oxidations are: methyl (72), ethyl (163, 251), *n*- and *sec*-propyl (35), and butyl radicals (34, 184).

Acyl radicals behave in a similar way; the effect is more pronounced because not even the nitro form is stable. Thus formyl (394) and acetyl (249) yield the corresponding formate and acetate radicals:

$$CH_3CO + NO_2 \rightarrow CH_3COO + NO$$

$$CH_3COO \rightarrow CH_3 + CO_2$$

At temperatures above 120°C. decomposition to alkyl and carbon dioxide follows.

Similar oxidation reactions occur with halogenated alkyl radicals. Thus the *n*-perfluoroalkyl radicals parallel exactly their organic counterparts.

$$C_3F_7 + NO_2 \rightarrow C_3F_7O + NO$$

$$C_3F_7O \rightarrow C_2F_5 + COF_2$$

$$C_2F_5 + NO_2 \rightarrow C_2F_5O + NO$$

and in addition to association, yielding perfluoronitroalkanes, they give the fluorine analog of formaldehyde (COF_2) and the corresponding lower radical (188).

Trichloromethyl radicals may be expected to behave similarly. For example, it is possible to account for the properties of the pyrolysis of chloropicrin by a reaction scheme of this type (163).

(c) Oxidation of molecules by nitrogen dioxide

Nitric oxide: Nitric oxide is "oxidized" by nitrogen dioxide, as is shown by the exchange reaction (228). Oxygen-atom transfer is rapid at room temperature and occurs through the intermediate form, ONONO, of dinitrogen trioxide. The activation energy of 10.5 kcal. probably represents the oxygen–nitrogen bond energy in dinitrogen trioxide.

Nitrogen dioxide: The reaction between nitric oxide and the nitrate radical is postulated in the schemes for the decomposition of dinitrogen pentoxide (208). The reverse reaction is, of course, an excellent though unusual example of oxygen-atom transfer:

$$NO_2 + NO_2 \rightleftharpoons NO + NO_3$$

Oxygen: The oxidation of oxygen to ozone is another reaction commonly observed in reverse (209). The thermodynamic properties of the species involved are well enough known for the forward reaction to be estimated.

$$NO_2 + O_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} NO + O_3$$

The reverse $k_r = 0.8 \times 10^{12} \exp(-2500/RT)$ cc. mole^{-1} sec.$^{-1}$, corresponding to a rate constant for the forward reaction $k_f = 1.2 \times 10^{12} \exp(-50{,}000/RT)$ cc. mole^{-1} sec.$^{-1}$ It is noteworthy that this corresponds to a "steric factor" of approximately 10^{-2}.

Nitrosyl chloride: The oxidation of nitrosyl chloride to nitryl chloride has been observed (287) in the presence of dinitrogen tetroxide:

$$NOCl + NO_2 \rightleftharpoons NO_2Cl + NO$$

Better investigated, however, is the reverse reaction (141), the rapid reduction by NO of NO_2Cl. For this (second-order) reaction $k = 0.83 \times 10^{12} \exp(-6900/RT)$ cc. mole^{-1} sec.$^{-1}$ It is interesting that the reaction path is ambiguous; transfer of either an oxygen or a chlorine atom can explain the change observed.

Carbon monoxide: The rate of this reaction in the gas phase has been measured in the range 528–800°K. with a large excess of carbon monoxide to prevent interference by the decomposition of nitrogen dioxide (101–104).

$$CO + NO_2 \rightarrow CO_2 + NO$$

The reaction was found to be first order with respect to each component with k (liter mole^{-1} sec.$^{-1}$) $= 4.8 \times 10^{8} \exp(-27{,}800/RT)$. In mixtures of carbon monoxide, oxygen, and nitrogen dioxide the formation of carbon dioxide is faster than this equation predicts and the species NO_3 has been suggested as an intermediate.

Sulfur dioxide: Stoichiometrically this reaction represents part of the operation of the lead chamber process for the manufacture of sulfuric acid.

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

At low temperatures, reaction is affected by surface area and by small amounts of water vapor (223). The reaction between the dry gases (63, 202, 223) is first order with respect to each component and in the temperature range 160–230°C. has $E_{\text{act.}} = 24{,}500$ cal. At temperatures below 150°C. (202) the overall activation energy is much less and initiation appears to be a heterogeneous process at the vessel wall in which water plays an important part.

Hydrogen chloride: The reaction between nitrogen dioxide and hydrogen chloride has been represented as follows (182):

$$NO_2(g) + 2HCl(g) \rightarrow NOCl(g) + \tfrac{1}{2}Cl_2(g) + H_2O$$

2. Reduction by nitrogen dioxide

$$NO_2 + ZO \rightarrow NO_3 + Z$$

Reactions in which nitrogen dioxide gains another atom of course include association and abstraction reactions (Sections VII,B and VII,D). A particular class of these, worthy of separate consideration, is the oxidation of nitrogen dioxide to dinitrogen pentoxide which proceeds *via* the intermediate NO_3. Examples include the reactions with ozone and with nitryl chloride, and the exchange reaction between N_2O_4 and N_2O_5. The oxidations to the corresponding nitryl halide by fluorine and chlorine may also be considered with this class.

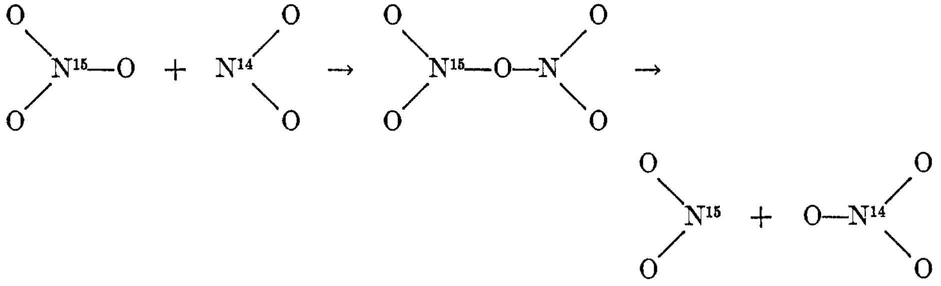
Ozone: The oxidation of nitrogen dioxide by ozone is a rapid reaction (212, 434) and is first order with respect to each reactant.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad \text{Rate-determining}$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad \text{Fast}$$

The final product is dinitrogen pentoxide. The velocity constant k in liter mole second units is given (212) by the expressions $k = 5.9 \times 10^9 \exp(-E/RT)$ or $3.5 \times 10^8 \sqrt{T} \exp(-E/RT)$ with $E = 7.0 \pm 0.6$ kcal. mole^{-1}.

Nitrogen trioxide, NO_3: The exchange reaction between $N^{14}_2O_4$ and $N^{15}_2O_5$ proceeds at the same rate as the decomposition of dinitrogen pentoxide; it is first order with respect to dinitrogen pentoxide and zero order with respect to dinitrogen tetroxide. Thus the mechanism is oxygen transfer between NO_2 and NO_3.



The reaction has been studied in both the gas phase and solution (284, 286).

Nitryl chloride, $ClNO_2$: The reverse reaction—the formation of nitrogen dioxide and nitryl chloride from nitrosyl chloride and nitrogen trioxide (as N_2O_5)—has been observed (287). This reaction has affinities with the N_2O_4–N_2O_5 exchange on the one hand and the NO_2–NOCl reaction on the other.

Fluorine, F_2: The reaction of nitrogen dioxide with fluorine is rapid; it is controlled by the rate of the step

$$NO_2 + F_2 \rightarrow FNO_2 + F \qquad \Delta H \sim 10 \text{ kcal.}$$

which is second order with k (liter mole^{-1} sec.$^{-1}$) $= 1.6 \times 10^9 \exp(-10{,}500/RT)$. All the fluorine atoms are removed by nitrogen dioxide to form more FNO_2.

Chlorine: The same reactions occur between chlorine and nitrogen dioxide (287); the formation of $ClNO_2$ in mixtures of chlorine and nitrogen dioxide has been observed. The reverse reaction, the decomposition of nitryl chloride, has been studied in detail (96). From this work the scheme for the reaction between nitrogen dioxide and chlorine may be written:

$$Cl_2 + NO_2 \rightarrow ClNO_2 + Cl$$

$$Cl + NO_2 \rightarrow ClNO_2$$

3. The decomposition of nitrogen dioxide

A species of oxygen transfer of course occurs in the reaction $2NO_2 \rightleftharpoons 2NO + O_2$. This reaction has been studied from equilibrium and kinetic standpoints (284, 286, 287, 306) as has the reverse reaction, the formation of nitrogen dioxide from nitric oxide (147) (Section II,E). The principle of detailed balancing permits information gained about the forward reaction to be used to supply knowledge about the reverse, and *vice versa.*

(a) The equilibrium $2NO_2 \rightleftharpoons 2NO + O_2$

Excellent thermodynamic data for the equilibrium are available (149) and may be summarized:

Equilibrium	ΔH_0^0	ΔH_{298}^0	ΔF_{298}^0	ΔS_{298}^0
$2NO_2 \rightleftharpoons 2NO + O_2$	25,542 cal.	27,124 cal.	16,750 cal.	34.80 cal.deg.$^{-1}$

The entropy ΔS^0 and free-energy function $(\Delta F^0 - \Delta H_0^0)/T$ have been evaluated as functions of temperature. Loosely speaking, it may be said that dissociation begins at 150°C. and is complete by 600°C.

(b) The reaction $2NO + O_2 \rightarrow 2NO_2$

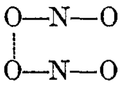
An account of this is given in Section VI,E, together with types of explanation which have been advanced to explain its principal properties—third-order kinetics and a rate constant diminishing with rise in temperature. The principal differences lay between a choice of consecutive second-order reactions and a triple collision (or trimolecular transition-state complex).

(c) The reaction $2NO_2 \rightarrow 2NO + O_2$

This reaction is homogeneous and second order (61, 62, 216) with

$$-d[NO_2]/dt = -k_2[NO_2]^2$$

In liter mole^{-1} sec.$^{-1}$ units, $k_2 = 8 \times 10^8 \exp(-25{,}000/RT)$ and the "steric factor" appears to be close to 10^{-2}. In terms of the classical collision-rate theory no specification of the transition state is made; in terms of the transition-state theory the picture must be the same as that of Gershinowitz and Eyring, *viz.*, I.



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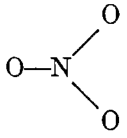

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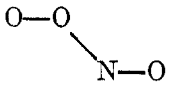


III

On the consecutive reaction theory, a slow formation of either $NO + NO_3$ or $O_2 + (NO)_2$ is required. Ambiguity does not end here, for NO_3 may be either the nitrate (II) or the pernitrite (III). Nitrate-radical formation clearly has an intermediate complex close to $ONONO_2$, while pernitrite-radical formation requires an intermediate ONOONO. These differ only in the orientation of the NO_2's at collision.

Identical problems are posed by the reactions

$$2NO_3 \rightleftharpoons 2NO_2 + O_2$$

and

$$2NOCl \rightleftharpoons 2NO + Cl_2$$

and when they are solved they will also add to our knowledge of the structure of dinitrogen tetroxide.

F. FLAMES SUPPORTED BY NITROGEN DIOXIDE

In recent years interest in nitrate monopropellants and in fuels of the type kerosene–nitric acid has drawn attention to the importance of oxidations and ignitions supported by nitrogen dioxide. Numerous investigations of spontaneous and spark ignitions have been made, but outstandingly the most valuable recent work is that of Wolfhard and Parker (295, 431) on stationary flames. Before outlining the properties of individual systems two general principles may be stated:

1. Except in flames with ammonia (and presumably hydrazine), pyrolysis to nitric oxide and oxygen precedes oxidation.
2. With simple fuels, e.g., hydrogen, oxidation by oxygen in the presence of nitrogen dioxide does not proceed beyond nitric oxide. With more complex fuels, e.g., hydrocarbons, there are two distinct reaction zones. In the first, reduction as far as nitric oxide proceeds; in the second, nitric oxide is itself reduced.

Among other systems the following fuels have received attention: hydrogen; carbon monoxide; carbon disulfide; C_nH_{2n+2}, where $n = 1$ to 5; ethylene and acetylene; formaldehyde; acetaldehyde; diethyl ether; methanol; ethanol.

1. Hydrogen–nitrogen dioxide

The spontaneous ignition limit has been measured as a function of temperature (31, 311) and flame speed in closed vessels measured (311). The stationary flame (295, 431) has been maintained at atmospheric pressure on a 1 mm. burner. Reaction proceeds only as far as nitric oxide:

$$NO_2 + H_2 \rightarrow NO + H_2O$$

A flame temperature of 1550°C. is reached. Thus the fastest flame occurs with a mixture ratio 1:1; its speed S_u is 260 cm. sec.$^{-1}$ relative to unburned gas. The emission spectrum shows OH and NO bands strongly and the NH band very weakly.

2. Carbon monoxide

Spontaneous ignition of carbon monoxide–nitrogen dioxide mixtures in the presence of hydrogen as sensitizer has been reported (75). The stationary flame (295, 431) has only one reaction zone, emitting continuous radiation. Its burning velocity S_u (cm. sec.$^{-1}$) is small (13–18) and affected by moisture. Reaction proceeds only as far as nitric oxide.

$$CO + NO_2 \rightarrow CO_2 + NO$$

3. Carbon disulfide

Liquid carbon disulfide and liquid nitrogen dioxide are miscible and together form an explosive "panclastite" which can be detonated by mercury fulminate

(405). Explosives of this type were first employed during the siege of Paris. The spark ignition of this system has been reported (46). Though complete oxidation corresponds to

$$CS_2 + 3NO_2 \rightarrow CO_2 + 2SO_2 + \tfrac{3}{2}N_2$$

the products include nitric oxide, carbon monoxide, sulfur, sulfur trioxide, and cyanogen.

4. Hydrocarbons

The spontaneous ignition of mixtures with nitrogen dioxide of the C_1 to C_5 normal paraffins has been examined in detail (436). Multiple flames paralleling the behavior of the oxygen systems are found; pressure and temperature limits for ignition have been mapped. Induction periods are eliminated by the addition of alkyl nitrites.

The stationary flames of similar mixtures with methane, acetylene, ethylene, and ethane have been investigated (295, 431). In all cases there are two reaction zones. The first emits only continuous radiation and appears identical with the single zone of the CO–NO_2 flame; the speed of this flame is less than 10 cm. sec.$^{-1}$ for methane. In the second zone nitric oxide is reduced to nitrogen, and CN, NH, and C_2 bands are emitted.

Typical maximum flame speeds, found are:

Species	C_2H_2	C_2H_4	C_2H_6
S_u (cm. sec.$^{-1}$)	135	46	20

They vary very little with pressure from 20 mm. to 1 atm., corresponding to a second-order reaction.

5. Alcohols, ethers, aldehydes

The spontaneous ignition of mixtures of formaldehyde and nitrogen dioxide has been reported (169, 315), and flame speeds in closed vessels have been measured (316). The maximum *spatial* velocity 1355 cm. sec.$^{-1}$ at 6 cm. total pressure occurs in a mixture containing 43 per cent formaldehyde (stoichiometric 41.5 per cent). The *calculated* flame temperature reaches a maximum of 2720°K.

Spontaneous ignition (169) and stationary flames (295) in acetaldehyde have been investigated. The flame structure has the same two zones as in hydrocarbons.

The spontaneous ignition of mixtures of methanol and ethanol has been described (169).

The structure of flames of ether with nitrogen dioxide parallels those of hydrocarbons. Novel features have been reported in the decomposition flame of methyl nitrate (165).

6. Ammonia

A spectroscopic study has been made of the ammonia–nitrogen dioxide diffusion flame (130). Some of the species that were identified are OH, NH, and NH_2 and the intensities of the first and second OH band heads, the NH lines, and the NH_2 lines are similar to those obtained in the ammonia–oxygen diffusion flame.

G. NITROGEN DIOXIDE AS A CATALYST: SENSITIZATION OF CHEMICAL REACTIONS AND EXPLOSIVE IGNITION

Small amounts of nitrogen dioxide can have a marked catalytic effect on a number of gas-phase reactions. The earlier work of Hinshelwood and Norrish was concerned with the reaction between hydrogen and oxygen sensitized by nitrogen dioxide, but data are now available for systems such as hydrocarbons, ethers, aldehydes, carbon monoxide, etc., and oxygen. In most instances the part played by the nitrogen dioxide depends on the following two reactions:

$$NO_2 \rightarrow NO + O \qquad (1)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (2)$$

In the first reaction oxygen atoms are formed either by thermal decomposition at temperatures of the order of 400–500°C. or photochemically. These oxygen atoms may then initiate and participate in chain reactions. Termination of chains may proceed according to equation 2, so that the effect of nitrogen dioxide will also depend on its concentration in the gaseous system. In addition, nitrogen dioxide may react with atoms or free radicals or with other molecules according to the scheme outlined in the previous sections.

1. Hydrogen–oxygen reaction

Small amounts of nitrogen dioxide when added to a hydrogen–oxygen mixture have a marked catalytic effect on both the slow reaction and ignition (109, 124, 134, 135, 151, 237, 277, 395). Concentrations of the order of 0.05 per cent may depress the ignition temperature by several hundred degrees. The catalytic action of the nitrogen dioxide is a function of the concentration; it goes through a maximum and falls again at high pressures of nitrogen dioxide. A reaction scheme for the sensitized ignition has been put forward by Norrish, Ashmore, and Dainton (276) and by Ashmore (31a).

The method of flash photolysis has been used by Norrish and Porter (278) to initiate the hydrogen–oxygen reaction in the presence of traces of nitrogen dioxide.

2. Carbon monoxide–oxygen reaction

This reaction is also sensitized by traces of nitrogen dioxide and behaves in a manner similar to the hydrogen–oxygen reaction (75, 345).

3. Combustion of hydrocarbons, ethers, and aldehydes

The effect of nitrogen dioxide on the oxidation of the higher hydrocarbons (119, 123, 136, 154, 214, 272, 281, 368, 369, 376, 377, 402, 407), ethers (82, 83, 215), and aldehydes (250) is complex. With these compounds cool flames can be obtained in addition to slow oxidation and explosive ignition, and the nitrogen dioxide alters each region differently. In general, addition of nitrogen dioxide catalyzes the explosion but acts as an inhibitor in the cool flame region. In the slow oxidation the presence of nitrogen dioxide lengthens the induction period of ether–oxygen and aldehyde–oxygen mixtures and in general promotes the reaction following the induction period, although the extent of this latter effect depends on the concentration of nitrogen dioxide.

The method of flash photolysis has been used to initiate the reaction between acetylene and oxygen (279) and between hydrocarbons and oxygen (280) in the presence of small amounts of nitrogen dioxide as sensitizer.

The influence of nitrogen dioxide on "knock" in internal combustion engines has been discussed by Downs, Walsh, and Wheeler (119).

H. PHOTOCHEMISTRY OF NITROGEN DIOXIDE

1. The absorption spectrum of nitrogen dioxide

The absorption spectrum of the gaseous equilibrium mixture in the visible region and as far as $\lambda = 2800$ Å. in the near ultraviolet is due to nitrogen dioxide. Numerous investigators (192) have described the principal features, which are summarized briefly (283, 341) in table 6.

2. Fluorescence of nitrogen dioxide

Fluorescence has been studied at pressures low enough for any contribution from dinitrogen tetroxide to be eliminated (43, 275). The ratio of the intensities of fluorescent to absorbed radiation is appreciable at $\lambda = 4360$ Å., weak at $\lambda = 4050$ Å., and virtually zero by $\lambda = 3650$ Å. (275). The following scheme for fluorescence at wavelengths from 3950 to 4360 Å. has been put forward:

$$\begin{array}{rl} NO_2 + h\nu \rightarrow NO_2^* & \quad I_a \\ NO_2^* \rightarrow NO_2 + h\nu' & \quad k_1 \\ NO_2^* + NO_2 \rightarrow 2NO_2 & \quad k_2 \end{array}$$

TABLE 6

The photochemistry of nitrogen dioxide: dependence of fluorescence, absorption, and quantum yield on wavelength

Wavelength	Fluorescence	Reaction	Absorption
Å.			
6000			Strong, discrete
4650	Strong	No reaction	
4360			
4050	Weak	Quantum yield = 0.5	
3950		$NO_2 \rightarrow NO + O(^3P)$	
3700			
3660	Absent	Quantum yield = 1.83	Diffuse
3130		Quantum yield = 1.93	
2800		Quantum yield = 2.0	
2650			
2596			Discrete
2459		↓	Diffuse
2450		$NO_2 \rightarrow NO + O(^1D)$	Diffuse

Application of the stationary-state principle yields

$$\frac{I_{\text{abs.}}}{I_{\text{fluorescent}}} = \frac{1}{k}\left(1 + \frac{k_2}{k_1}[\mathrm{NO_2}]\right)$$

in agreement with the experimental result (43) that I_a/I_f varies linearly with $[\mathrm{NO_2}]$.

The constant k_2 involves the collision frequency and if the lifetime of the excited state may be measured, an effective collision cross-section may be ascribed to the excited species. A direct measurement of the lifetime of this state has recently been made (271). Pressures of nitrogen dioxide down to 10^{-3} mm. have been illuminated by 5 μ sec. flashes of light. The predicted linear variation of fluorescence *vs.* pressure is found; extrapolation of the results to zero pressure gave for the mean lifetime, τ, a value of 4.5×10^{-5} sec. in the absence of collisions. The lifetime is the same for excitation by different (λ = 3950 Å., 4300 Å., 4650 Å.) exciting radiations. The fluorescent emission is a continuous radiation (when self-absorption is allowed for) extending up to 8000 Å.

3. Photolysis of nitrogen dioxide

The absorption of radiation and the formation of excited nitrogen dioxide molecules is marked by 6000 Å. This energy of excitation is not enough to dissociate the molecule and it is either quenched or re-radiated as fluorescence. At shorter (4000 Å.) wavelengths the absorption becomes diffuse and fluorescence fades as dissociation begins. The reaction is:

$$\mathrm{NO_2} + h\nu \rightarrow \mathrm{NO} + \mathrm{O}(^3P) \qquad \Delta H \sim 70{,}000 \text{ cal.}$$

Because of the competition from fluorescence and quenching the quantum yield is small (114, 198, 275). As the wavelength is further diminished and the energy of excitation increased, dissociation predominates; the intensity of fluorescence is zero by 3650 Å., absorption is continuous, and the quantum yield approaches 2. This leads to the second step:

$$\mathrm{NO_2} + \mathrm{O}(^3P) \rightarrow \mathrm{NO} + \mathrm{O_2} \qquad \Delta H \sim 45{,}000 \text{ cal.}$$

and a total change of two molecules of nitrogen dioxide decomposed per quantum absorbed. That absence of fluorescence is a better guide to the onset of reaction than is diffuse absorption is clearly shown by the second region of sharp absorption bands near 2596 Å. The second diffuse region near 2459 Å. corresponds to dissociation into nitric oxide and an excited oxygen atom (192).

$$\mathrm{NO_2} + h\nu \rightarrow \mathrm{NO} + \mathrm{O}(^1D)$$

In time, a photostationary state is set up as the recombination reaction sets in (275), but this is so slow at the low pressures employed as often to be negligible.

In solution in carbon tetrachloride, quantum yields are far smaller than in the gas phase (198). This has been ascribed to the deactivating collisions with the solvent molecules (Franck–Rabinowitch principle).

VIII. The Dinitrogen Tetroxide Solvent System

A. GENERAL PRINCIPLES

As described in Section IV,B, pure liquid dinitrogen tetroxide is stable (under atmospheric pressure) from the freezing point, −11.2°C., to the boiling point, +21.15°C. The cryoscopic constant K_f (100 g.) is 36.6°C.; the ebullioscopic constant K_b (100 g.) is 13.7°C. Homolytic dissociation to nitrogen dioxide is very small (the concentration of nitrogen dioxide is less than 1 per cent). The concentration of any ionic species is even less, as is shown by the very low electrical conductivity.

B. DINITROGEN TETROXIDE AS SOLVENT AND SOLUTE

1. Inert inorganic solutes

No simple inorganic salts are soluble in liquid dinitrogen tetroxide; solubilities follow those in ether (139). Some non-metallic elements dissolve freely: bromine is miscible in all proportions, iodine is freely soluble, and sulfur slightly so. Chlorine dissolves and undergoes slow reaction. Complete freezing-point data are available (table 7) for mixtures of dinitrogen tetroxide with nitrosyl chloride (25), dinitrogen trioxide (41, 205, 303, 420, 430), dinitrogen pentoxide (243), and sulfur dioxide (362a).

Nitrogen dioxide is also miscible with carbon disulfide (107, 143, 333) and with silicon tetrachloride (107).

2. Organic solutes yielding simple solutions

Many organic compounds dissolve readily without reaction and may be recrystallized from solution. Thus the following substances have been listed (73, 139): saturated aliphatic hydrocarbons; aromatic hydrocarbons (benzene, toluene); halogen compounds (ethyl bromide, ethylene dichloride, ethylene dibromide, acetylene tetrabromide, chloroform, bromoform, carbon tetrachloride, methyl iodide, benzyl chloride, chloro- and bromobenzene); nitro compounds

TABLE 7

The N_2O_4 *solvent system: eutectic compositions and temperatures*

Binary Mixture with	Eutectic Temperature	N_2O_4
	°C.	*weight per cent*
N_2O_3	−107	—
N_2O_5	−15.8	10.8
NOCl	−74.8	41.3 ($N_2O_4 \cdot 2NOCl$)
SO_2	−84.2	9.35 ($N_2O_4 \cdot 12SO_2$)
CH_3NO_2	−56	47
CCl_3NO_2	−79.5	8
CH_3I	−69.5	10
$CHBr_3$	−13.5	66.5
$CHCl_3$	−68	8.5
CCl_4	−49	8.15
C_6H_5Br	−42.5	14
2,4,6-$(NO_2)_3C_6H_2CH_3$ (T.N.T.)	−13.5	61
1-OH-2,4,6-$(NO_2)_3C_6H_2$ (picric acid)	−17	60.6

(nitromethane, chloropicrin, nitrobenzene, nitroethane, *m*-dinitrobenzene, *p*-nitrotoluene, and 1,5-dinitronaphthalene); quinones (benzoquinone and anthraquinone); nitrophenols (2,4-dinitrophenol and picric acid); and many carboxylic acids (formic, acetic, chloroacetic, trichloroacetic, tribromoacetic, trichlorobutyric; malonic, succinic; benzoic, *o*-, *m*-, and *p*-toluic, *m*-nitrobenzoic, phthalic, and 5-nitrosalicylic).

Conductivity measurements show that dinitrogen tetroxide is not an ionizing solvent, and cryoscopic measurements reveal that carboxylic acids are associated to double molecules.

The phase diagrams of a number of binary systems are available (12, 302). Systems yielding simple eutectics are listed in table 7. They range over a wide variety of compositions and temperatures.

C. SELF-IONIZATION IN PURE LIQUID DINITROGEN TETROXIDE

Clusius and Vecchi (90) elegantly demonstrated the occurrence of ionization:

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

They prepared tetramethylammonium N^{15}-nitrate and dissolved it in excess dinitrogen tetroxide. Exchange was found to be complete. Stoichiometrically, of course, ionization is extremely small; the low dielectric constant ($\epsilon = 2.4$) does not favor dissociation. No evidence has been found for ionization to NO_2^+ and NO_2^-.

D. DINITROGEN TETROXIDE IN SOLVENTS OF HIGH DIELECTRIC CONSTANT

In the pure liquid (dielectric constant, ϵ, equals 2.4) the specific conductivity is 1.3×10^{-12} mho. In nitromethane (dielectric constant, ϵ, equals 37) a 10^6-fold increase is found, though ionization is still small. In mixtures of acetic and nitric acids dinitrogen tetroxide behaves as a weak electrolyte, yielding NO^+ in small concentration; the conductivity of dinitrogen tetroxide dissolved in nitric acid is about the same as that of potassium nitrate, a moderately strong electrolyte in that solvent; in sulfuric acid ($\epsilon \sim 110$) ionization to NO^+ is complete.

Similarly, dinitrogen tetroxide dissolved in absolute perchloric acid (177) yields nitrosyl perchlorate, $NOClO_4$; in phosphoric acid, nitrosylphosphoric acid (139, 441); and in pyrosulfuric acid, nitrosyl pyrosulfate (39, 206). The derivatives $NOBF_4$, $NOReO_4$, and $NOHSeO_4$ are also well known (20, 264). The acid solvents which have been most completely investigated are nitric and sulfuric acids.

In nitric acid, Raman spectroscopy (160) shows that the species N_2O_4 is completely absent. The strongest line (2240 cm.$^{-1}$) belongs to NO^+. No spectroscopic evidence for NO_2^+ or NO_2^- is found, though NO_2 is present (see, however, 245). Addition of alkali metal nitrates to this solution increases the vapor pressure above the solution, an effect easily explained by displacement of the ionic equilibrium. Dinitrogen tetroxide and nitric acid are not completely miscible over the whole composition range; the phase relations have been reported in old (65, 205, 219, 303) and new (95) papers.

In concentrated sulfuric acid cryoscopic work (152) has revealed in dilute solution a sixfold depression of the freezing point in accord with the equations:

$$N_2O_4 + H_2SO_4 \rightarrow NO^+ + HSO_4^- + HNO_3$$

$$HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + NO_2^+ + 2HSO_4^-$$

Sulfuric acid is such a strong proton-donor that it converts nitric acid quantitatively into NO_2^+ at these low concentrations; however, in a solution containing 20 mole per cent dinitrogen tetroxide, molecular HNO_3 is observed (259; see also 195a).

E. COMPOUND FORMATION IN THE DINITROGEN TETROXIDE SOLVENT SYSTEM

Compound formation has been reported in liquid mixtures of dinitrogen tetroxide with tertiary amines, ethers, nitriles, etc. (7, 9, 13, 20, 33a, 150, 239, 343, 419). They have been investigated by the classical methods of cryoscopy, conductivity, viscosity, etc.; no structural investigation has been completed. The various compounds recognized are listed in table 8.

1. Compounds with tertiary amines and similar systems

Complexes of the general formula $N_2O_4 \cdot B$ and $N_2O_4 \cdot 2B$, where B stands for the base, have been observed between tertiary amines and dinitrogen tetroxide. These complexes are colored (aliphatic, brown; aromatic, plum (93, 94)); they are insoluble in hydrocarbons but soluble in halogen derivatives and in ether. They are stable only at low temperatures. Complexes of aromatic heterocyclic nitrogen compounds (110) form yellow precipitates from ethereal solution.

TABLE 8

The dinitrogen tetroxide solvent system: compound formation with oxygen and nitrogen compounds

Oxygen Derivatives	Number of Molecules of Base in Compound Formed	Nitrogen Derivatives	Number of Molecules of Base in Compound Formed	Nitriles and Ketones	Number of Molecules of Base in Compound Formed
Diethyl ether	2	Trimethylamine	1, 2	Acetonitrile	1, 2
Di-*n*-propyl ether	2	Triethylamine	2	Benzonitrile	1
Diisopropyl ether	2	Diethylnitrosoamine	2		
Di-*n*-butyl ether	2	Dimethylaniline	1, 2	Acetone	2
Di-*tert*-butyl ether	None	Diethylaniline	2	Camphor	$\frac{4}{5}$, $\frac{3}{2}$
		N-Methyldiphenylamine	2		
Tetrahydrofuran	1*, 2	*o*-, *m*-, and *p*-Nitrodimethylaniline	None	Acetic acid	2
α-Methyltetrahydrofuran	2				
Perfluorotetrahydrofuran	None	*p*-Nitrosodimethylaniline	2	Acetic anhydride	1
Tetrahydropyran	2	Pyridine	2		
		α-Picoline	1, (2)		
Ethylene glycol diethyl ether	1	β-Picoline	1, (2)	Ethyl benzoate	2
1,4-Dioxane	1	2,6-Lutidine	None		
1,3-Dioxane	1	Quinoline	2		
Trioxane	1	2-Methylquinoline	None		
		Isoquinoline	2		
		Acridine	2		

* Incongruent melting point.

An equilibrium of the type

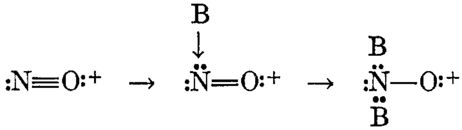
$$\mathrm{N_2O_4\cdot 2B} \overset{a}{\rightleftharpoons} \mathrm{N_2O_4\cdot B} + \mathrm{B} \overset{b}{\rightleftharpoons} \mathrm{N_2O_4} + \mathrm{2B}$$

exists for the addition compounds. All the bases studied form complexes of the type $N_2O_4\cdot 2B$; the species $N_2O_4\cdot B$ has not been found for all. Equilibrium *a* lies to the right for the picolines but to the left for other heterocyclic compounds.

Compounds which do not give such complexes are *o*-, *m*-, and *p*-nitrodimethylaniline, α,α'-lutidine, and 2-methylquinoline (110). Steric hindrance has been advanced as the factor preventing complex formation by the three heterocyclic compounds.

Included in the list of complexing bases is diethylnitrosoamine, which has been made the subject of special study by Addison *et al.* (7, 9, 13, 20). Its behavior justifies its inclusion with the tertiary amines.

On the basis of measurements of electrical conductivity and absorption spectra Comyns (93, 94) ascribes the formula $R_3N\cdot NO^+NO_3^-$ to the compound. Addison (7, 13, 20) explains the addition compounds $N_2O_4\cdot B$ and $N_2O_4\cdot 2B$ as due to the coördination of one and two B molecules, respectively, to the nitrosonium ion of the $NO^+NO_3^-$ ion-pair; donation of electron pairs occurs in two stages:



$$:\mathrm{N}{\equiv}\mathrm{O}:^{+} \rightarrow \overset{\overset{\displaystyle \mathrm{B}}{\downarrow}}{:\ddot{\mathrm{N}}}{=}\mathrm{O}:^{+} \rightarrow \underset{\displaystyle \mathrm{B}}{\overset{\displaystyle \mathrm{B}}{:\ddot{\underset{..}{\mathrm{N}}}}}{-}\mathrm{O}:^{+}$$

The stability of the species depends on the nature of the base B and on external conditions such as the temperature and the solvent medium. The influence of the nature of the base is clearly shown by the existence of bases which do not form addition compounds: the three nitrodimethylanilines presumably because of mesomeric effects, and the lutidines because of steric blocking of the nitrogen atom. Solvolysis by ether of, for example, the pyridine complexes is unimportant; the ether complex is largely dissociated even at −35°C. The compounds are analogous to the base-stabilized halogen nitrates $(C_5H_5N)_2BrNO_3$ and $(C_5H_5N)_2ClNO_3$.

The nitrosonium-ion vibration frequency is so altered in nitric acid solutions of dinitrogen tetroxide that Goulden and Millen (160) have proposed for it a formula of the type $NO_2\cdot NO^+$; it may be that N_2O_4 itself can act as a complexing agent for the ion NO^+. If a compound has to be assumed, there is no evidence which favors $NO_2\cdot NO^+$ more than, for example, $N_2O_4\cdot NO^+$.

2. Compounds with ethers and other oxygen derivatives

Addition compounds of the type $N_2O_4\cdot 2B$ are also formed with ethers and other oxygen derivatives (343, 419) and melting points and phase diagrams recorded. With diethers such as dioxane or ethylene glycol diethyl ether the general formula is $N_2O_4\cdot B$ (239, 343, 419). The shapes of the freezing-point curves indicate that the compounds exist in the liquid phase. Sisler and coworkers conclude that the complexes are molecular addition complexes of the Lewis acid–Lewis base type in which the oxygen of the ether is the basic center. No x-ray data are available to confirm this suggestion, but spectroscopic measurements are stated to have failed to reveal the presence of NO^+; otherwise, the formulation adopted for the addition compounds with tertiary amines is more attractive. The formulas based on two coördinated oxygen atoms per nitrosonium ion satisfy the observations.

Perfluorotetrahydrofuran and di-*tert*-butyl ether fail to give addition compounds (419). It may be supposed that the electron distribution at the oxygen atom of the former is inadequate, owing to the effect of the eight fluorine atoms (419), and that the two four-carbon groups of the latter are too bulky, although the electron distribution should be suitable.

3. Compounds with nitriles and ketones

Acetonitrile and benzonitrile also form addition compounds (13). Acetonitrile forms both $N_2O_4 \cdot CH_3CN$ and $N_2O_4 \cdot 2CH_3CN$, while benzonitrile yields $N_2O_4 \cdot C_6H_5CN$ only. The formulas are supposed to be similar to the nitrogen complexes, with the unshared electrons of the cyanide group being donated to the nitrosonium ion.

Acetone reacts with liquid dinitrogen tetroxide (presumably by an enolic form) at low temperatures, yielding a complex mixture of reaction products among which cyanides, nitrates, and nitro compounds have been found (437). At low temperatures however (−40°C.), a compound $N_2O_4 \cdot 2(CH_3)_2CO$ is formed (20). Camphor gives two compounds (302) with compositions corresponding to the formulas $5N_2O_4 \cdot 4C_{10}H_{16}O$ (m.p., −52°C.) and $2N_2O_4 \cdot 3C_{10}H_{16}\ O$ (m.p., −45.5°C.). No explanation for the stoichiometry has been offered.

F. COMPLEX SALT FORMATION IN THE DINITROGEN TETROXIDE SYSTEM

A number of addition complexes with inorganic compounds, some known for many years (156) and others only recently reported (20), throw further light on the ionization in the dinitrogen tetroxide system. Among the most thoroughly investigated (15) is the product of reaction between zinc nitrate (or zinc metal or zinc oxide) and dinitrogen tetroxide, $Zn(NO_3)_2 \cdot 2N_2O_4$. Its formula has been shown to be $(NO^+)_2[Zn(NO_3)_4^{2-}]$. Similarly, the uranyl nitrate complex $UO_2(NO_3)_2 \cdot N_2O_4$ may be set as the nitrosonium salt of the better known (11)

TABLE 9

Complex salt formation in the dinitrogen tetroxide solvent system

Conventional Formula	Nitrosonium Derivative	Conventional Formula	Nitrosonium Derivative
$Zn(NO_3)_2 \cdot 2N_2O_4$	$(NO)_2[Zn(NO_3)_4]$	$4FeCl_2 \cdot NO_2$	
$UO_2(NO_3)_2 \cdot 2NO_2$	$(NO)[UO_2(NO_3)_3]$	$4FeBr_2 \cdot NO_2$	
$BiCl_3 \cdot NO_2$		$FeCl_3 \cdot NO_2$	
$2TiCl_4 \cdot 3N_2O_4$		$PF_5 \cdot NO_2$	
$2SnCl_4 \cdot 3N_2O_4$		$AsF_5 \cdot NO_2$	
$3SnCl_4 \cdot 2N_2O_4$		$2AlCl_3 \cdot 3C_6H_6 \cdot 3N_2O_4$	
$3SbCl_5 \cdot 2NO_2$		$FeCl_3 \cdot 2C_6H_6 \cdot 2N_2O_4$	
$SbF_5 \cdot NO_2$	$(NO^+)(SbF_4^+)(SbF_6^-)_2$	$SnCl_4 \cdot 2C_6H_6 \cdot 2N_2O_4$	

trinitrato uranyl ion, *viz.*, $NO^+[UO_2(NO_3)_3^-]$. Recently, the addition compounds $NO_2 \cdot AsF_5$ and $NO_2 \cdot SbF_5$ have been described, and they may possess the general formula $NO^+ \cdot MF_4^+(MF_6^-)_2$.

A list of complexes is given in table 9. Included in it are three interesting organometallic derivatives of a type familiar in studies of Friedel–Crafts catalysts.

IX. The Reactions of Dinitrogen Tetroxide

A. GENERAL PRINCIPLES

In Section VIII the tendency of dinitrogen tetroxide to ionize as NO^+ and NO_3^- emerged clearly. This tendency is detectable even in the pure liquid. Different factors which assist it are the following: solvents of high dielectric constant (e.g., sulfuric acid) and great ionizing power; solutes which by removing NO_3^- into an anionic complex (e.g., $Zn(NO_3)_2 \rightarrow Zn(NO_3)_4^{2-}$) form free NO^+; solutes which by coördination stabilize the actual cation (e.g., $2R_3N + N_2O_4 \rightarrow (R_3N)_2NO^+\ NO_3^-$). No similar grounds for ionization to NO_2^+ and NO_2^- have been found.

Of course, ionization is often only incipient and we may consider an ion-pair as having been formed rather than separate ions. Frequently, secondary reactions lead to changes much more profound than ionization. Thus, water is a solvent with a high dielectric constant, but reaction does not stop with the formation of NO^+. Instead, NO^+ reacts with water, forming hydrogen ions and nitrous acid; the nitrous acid itself decomposes, and so on. In all such reactions, however, whether with water or with alcohols, ammonia, or amines, the evidence for NO^+ is strong.

The second complication occurs in the presence of a ready donor of electrons (reducing agent). Then the products of reaction are no longer NO_3^- and NO^+ but NO_3^- and NO. To this class belong the metals and anions which react readily with dinitrogen tetroxide at low temperatures:

$$N_2O_4 + M \rightarrow NO + NO_3^- + M^+ \text{ (i.e., } MNO_3)$$

$$N_2O_4 + X^- \rightarrow NO + NO_3^- + X(\tfrac{1}{2}X_2)$$

In the reactions which follow, that with water is dealt with most fully because of its immense technical importance.

B. THE REACTION BETWEEN DINITROGEN TETROXIDE AND WATER

This reaction occurs in the manufacture of nitric acid by the absorption of nitrous gases. The system is complex; chemical equilibria, reaction kinetics and, to a smaller extent, physical aspects of absorption all play a part. The interpretation of the system is based principally on the work of Abel (1) and of Denbigh (80, 111).

1. The phase diagram

Dinitrogen tetroxide and water form two liquid phases over a wide range of composition (243, 244): the upper layer is largely aqueous nitric acid; the lower layer is deep blue owing to the presence of dinitrogen trioxide. At 0°C. the limits of miscibility are 47 and 98 weight per cent dinitrogen tetroxide and at 20°C., 52 and 98. At the consolute temperature, 67°C., there is 89 weight per cent dinitrogen tetroxide. The phase diagram is complex. Homogeneous aqueous solutions deposit ice at temperatures down to −50°C. and compositions containing 0–33 weight per cent dinitrogen tetroxide; the composition of the solid phase deposited between −50° and −56°C. from solutions containing 33–44 weight per cent dinitrogen tetroxide is not known. Homogeneous mixtures containing more than 44 weight per cent dinitrogen tetroxide deposit nitric acid trihydrate, $HNO_3 \cdot 3H_2O$, from the upper aqueous layer and dinitrogen tetroxide from the lower layer (mixed $N_2O_4 + N_2O_3$).

Data for the density, solubility, and boiling points of N_2O_4–HNO_3 mixtures (65, 95, 205, 219, 303) and for the properties of fuming nitric acid (65, 219) are also available.

2. Stoichiometry and chemical equilibria

When dinitrogen tetroxide is dissolved in a large excess of water nitrous and nitric acids are formed in equal amounts:

$$N_2O_4 + H_2O = HNO_2 + H^+ + NO_3^-$$

Nitrous acid is a weak acid ($K_A = 6 \times 10^{-4}$ at 30°C.) (218, 358). The unionized acid decomposes into nitric acid and nitric oxide, though only slowly at low temperatures, until equilibrium is reached:

$$\begin{array}{rcl} 3N_2O_4 + 3H_2O & = & 3HONO + 3H^+ + 3NO_3^- \\ 3HONO & = & H_2O + H^+ + NO_3^- + 2NO \\ \hline 3N_2O_4 + 2H_2O & = & 2NO + 4H^+ + 4NO_3^- \end{array}$$

All the reactions are reversible. Thus, the nitric oxide formed in the decomposition of the nitrous acid reduces the equilibrium concentration of nitric acid attainable with a given pressure of dinitrogen tetroxide. Abel has measured the equilibrium constant of the overall reaction. Table 10 lists values of the equilibrium constant expressed in terms of partial pressures of the species HNO_3, H_2O, NO, and NO_2.

TABLE 10

Equilibrium constants for the gas-phase reaction between water and nitrogen dioxide (137)

$$H_2O + 3NO_2 = 2HNO_3 + NO$$

$$\Delta H_0^0 = -7230 \text{ cal.}$$

$$K = P_{HNO_3}^2 P_{NO} / P_{H_2O} P_{NO_2}^3$$

Temperature	Equilibrium Constant, K	Temperature	Equilibrium Constant, K
°C.	*atm.*$^{-1}$	*°C.*	*atm.*$^{-1}$
275	3.75×10^{-2}	350	1.01×10^{-3}
293.1	1.37×10^{-2}	400	1.87×10^{-4}
298.1	1.05×10^{-2}	450	4.86×10^{-5}
300	9.51×10^{-3}	500	1.65×10^{-5}

TABLE 11

Equilibrium data (137) for the gas-phase reaction

$$2NO_2 + H_2O + \tfrac{1}{2}O_2 = 2HNO_3$$

$$\Delta H_0^0 = -20{,}025 \text{ cal.}$$

$$K\ (\text{atm.}^{-3/2}) = P^2_{HNO_3}/(P^2_{NO_2}P_{H_2O}P^{1/2}_{O_2})$$

Temperature	K	Temperature	K
°C.	*atm.*$^{-3/2}$	*°C.*	*atm.*$^{-3/2}$
275	3.65×10^5	400	4.43×10^{-1}
298.1	1.45×10^4	450	2.81×10^{-2}
300	1.13×10^4	500	2.06×10^{-3}
350	4.65×10		

Clearly, since P_{HNO_3} and P_{H_2O} are determined by the concentration of the nitric acid,[2] so is the ratio $P_{NO}/P^3_{NO_2}$. At 25°C. this quotient in atm.$^{-2}$ $P_{NO}/P^3_{NO_2}$ has the values 2.75×10^4 for 37 per cent acid and 1.00×10^2 for 58.8 per cent acid. For more concentrated acid the quotient is smaller, and very little nitric oxide is necessary to prevent the absorption of further dinitrogen tetroxide. In industrial practice the formation of acid much stronger than 50 per cent is too slow at atmospheric pressure to be worth while. Higher concentrations are achieved by employing a mixture of air and nitrogen dioxide, the oxygen serving to convert the nitric oxide formed to nitrogen dioxide. This oxidation (see Section II,E) is very slow, however. Acid of 62–66 per cent strength is made in systems operated at 6 atm. pressure.

Very strong (nearly 100 per cent) nitric acid has been produced by compressing mixtures of oxygen, water, and liquid dinitrogen tetroxide to 20–65 atm. (Hoko process).

$$2N_2O_4 + O_2 + 2H_2O \rightarrow 4HNO_3$$

The equilibrium data (137) are listed in table 11. However, concentrated nitric acid is more commonly made by distilling 50 per cent nitric acid. The azeotropic mixture (68.4 per cent HNO_3, b.p. 121.9°C.) can be made directly; 100 per cent nitric acid is made by distillation with sulfuric acid. These acids as made contain dissolved oxides of nitrogen produced by decomposition during distillation. They may be "bleached" by a stream of air.

3. Kinetics of the reaction between dinitrogen tetroxide and water

From a kinetic viewpoint the measured rate of reaction of dinitrogen tetroxide with water is the difference in the rates of the forward and reverse reactions:

$$N_2O_4 + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} HONO + H^+ + NO_3^-$$

Abel (1) has solved the problem of the decomposition of nitrous acid, and Denbigh has shown that Abel's interpretation also explains the problem here.

---

[2] The necessary partial pressure data are provided by Forsythe and Giauque's (137) critical review of existing data (387, 408, 426). For a recent commentary see reference 435.

Abel discovered that in the system N_2O_4, N_2O_3, NO_2, NO, H_2O, HONO, H^+, and NO_3^- the reactions involved in the equilibria:

$$4HNO_2 \rightleftharpoons 2H_2O + 2N_2O_3$$

$$2N_2O_3 \rightleftharpoons 2NO + 2NO_2 \rightleftharpoons 2NO + N_2O_4$$

are much more rapid than those involved in

$$N_2O_4 + H_2O \rightleftharpoons HONO + H^+ + NO_3^-$$

and that the rate of the decomposition of nitrous acid, which obeyed a complicated kinetic expression, was identically its net rate of transformation into dinitrogen tetroxide (1). For the reaction of dinitrogen tetroxide with water the exact converse is true, and its rate of disappearance should obey the equation:

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

Now if the mobile equilibria above are maintained

$$[HNO_2] = [N_2O_4]^{\frac{1}{4}}[NO]^{\frac{1}{2}}[H_2O]^{\frac{1}{2}}$$

and we have

$$\begin{aligned} -\mathrm{d}[N_2O_4]/\mathrm{d}t &= \frac{3}{4}k_f[H_2O]\left\{[N_2O_4]\,\frac{k_r[HNO_3]}{k_f[H_2O]^{\frac{1}{2}}}\,[N_2O_4]^{\frac{1}{4}}[NO]^{\frac{1}{2}}\right\} \\ &= k_a\{[N_2O_4] - C[N_2O_4]^{\frac{1}{4}}[NO]^{\frac{1}{2}}\} \end{aligned}$$

where C is *not* an arbitrary constant but is completely determined by thermodynamic constants of the system.

This is exactly the experimental equation found by Denbigh and Prince (for C they give a useful explicit formula and tables of values). The test of their equation is constancy of k_a, which is satisfied very well. It is worthy of note that, at atmospheric pressure, increased temperature diminishes the gas-phase concentration of dinitrogen tetroxide and hence the rate of absorption in water.

The complex expressions written above have an extremely simple interpretation in terms of the ionization of dinitrogen tetroxide. Since

$$[H^+][HONO] = \text{const.}[H_2NO_2^+] = \text{const.}[NO^+][H_2O]$$

therefore

$$-\mathrm{d}[N_2O_4]/\mathrm{d}t = \text{const.}[N_2O_4] - \text{const.}[NO^+][NO_3^-]$$

or

$$= \text{const.}[N_2O_4][H_2O] - \text{const.}[H_2NO_2^+][NO_3^-]$$

where $H_2NO_2^+$ is the nitrous acidium ion. Set in this form, the rate of reaction of dinitrogen tetroxide with water is seen to be determined by its net rate of ionization.

4. Kinetics of the reaction between dinitrogen tetroxide and dilute aqueous alkali and the initial rate of absorption in water

In the presence of dilute alkali reaction is no longer reversible but is instead represented by the equations

$$N_2O_4 + H_2O \rightarrow HONO + H^+ + NO_3^- \qquad \text{Slow} \qquad (1)$$

$$HONO + OH^- \rightarrow NO_2^- + H_2O \qquad \text{Fast} \qquad (2)$$

$$H^+ + OH^- \rightarrow H_2O \qquad \text{Fast} \qquad (3)$$

Equation 1 still controls the rate of reaction, i.e.,

$$-d(N_2O_4)/dt = k_f[N_2O_4][H_2O]$$

or in terms of k_a

$$\text{Rate} = {}^4\!/_3 k_a[N_2O_4]$$

Absorption into 10 per cent alkali does obey this equation with k_a (observed) within a few per cent of the expected value.

Exactly the same expression governs the *initial* rate of reaction with water, before the concentration of nitrous acid has had time to build up and the acid to undergo appreciable decomposition.

5. Kinetics of reaction in the presence of nitric oxide

Added nitric oxide does not affect the actual reaction discussed above, but by forming dinitrogen trioxide it gives rise to a new reaction: namely, the rapid reaction of the dinitrogen trioxide species with water and the absorption of a much greater amount of nitrogen dioxide into alkaline solutions per unit time. In fact, this reaction occurs so much more rapidly that virtually no nitrate ions are formed (416, 417):

$$N_2O_3 + H_2O \rightarrow 2HONO$$

$$2HONO + 2OH^- \rightarrow 2H_2O + 2NO_2^-$$

In the absence of alkali, the equilibria mentioned above have already taken into account the final effect of nitric oxide; initially, there is an enhanced rate of formation of nitrous acid but not, of course, of nitrate ion.

The reaction which occurs between nitric oxide and aqueous nitric acid (i.e., nitrate ion) in the initial absence of nitrogen dioxide has been mentioned briefly (111); the gas-phase reaction has also been investigated both under conditions in which the surface is important (372) and when reaction is homogeneous (210). This last study at high temperatures is not a reaction of dinitrogen tetroxide but of nitrogen dioxide as a free radical.

6. The location of reaction in absorption towers

Industrially the reaction between nitrogen dioxide and water is carried out in absorption towers. Though some reaction can (and does) occur in the gas phase (for example, when streams of dinitrogen tetroxide and water vapor meet, a nitric acid mist forms), reaction occurs principally in the surface layers of the liquid. The following observations confirm this view: (*1*) The rate of absorption is proportional to the interfacial area and does not depend on the volume of the gas phase. (*2*) Concentrations in the gas phase can readily be calculated and are far too small for the diffusion of gaseous products to explain the observed rate. (*3*) When an alkaline absorbent is used, though the gas-phase composition is still water vapor, no nitric oxide is formed; hence, gas-phase reaction plays a negligible part. Nevertheless an attempt has been made to explain the absorption of nitrous gases in terms of physical diffusion after gas-phase reaction. For the reasons just mentioned, it is not satisfactory; furthermore, this theory (84) predicts the wrong dependence of rate on concentration of dinitrogen tetroxide (80, 111). However, the state of the surface layers is important, and flow speeds of liquid and gas affect absorption coefficients. Thus, increasing the gas flow from Reynolds number $R_e = 4{,}450$ to 11,100 (150 per cent increase) increased the coefficient k_a by 20–30 per cent; increasing the liquid flow from $R_e = 140$ to $R_e = 320$ (120 per cent increase) increased k_a by some 30 per cent.

C. THE REACTION OF DINITROGEN TETROXIDE WITH ALCOHOLS

1. Stoichiometry and chemical equilibria

The reaction of dinitrogen tetroxide with alcohols parallels that with water. The general equation was formulated correctly by Gray and Yoffe (438) as the equilibrium:

$$\mathrm{ROH} + \mathrm{N_2O_4} \rightleftharpoons \mathrm{RONO} + \mathrm{H^+} + \mathrm{NO_3^-}$$

In the gas phase a mist of nitric acid vapor is formed; in solution, two liquid layers separate, one rich in nitric acid, the other in nitrite ester. Use of isotopically labelled alcohols (26, 27, 346) has shown that reaction again involves the formation of the ionic species $\mathrm{NO^+}$:

$$\mathrm{RO^{18}H} + \mathrm{NO^+NO_3^-} \rightleftharpoons \mathrm{RO^{18}NO} + \mathrm{H^+} + \mathrm{NO_3^-}$$

It may be noted that the rapid esterification of alcohols by nitrous acid or nitrous anhydride takes place under conditions favorable to the formation of $\mathrm{NO^+}$ (346).

Measurements of the concentration of nitrogen dioxide in the equilibrium system have been used in conjunction with the equation above in an attempt to derive thermodynamic functions for the alkyl nitrites. At present experimental difficulties arising from absorption and, at temperatures above 25°C., secondary reactions have frustrated these intentions (127).

2. Chemical kinetics of the homogeneous gas-phase reaction

Kinetic measurements of the rate of gas-phase reaction between dinitrogen tetroxide and methyl, ethyl, *n*-propyl, and *tert*-butyl alcohols have been reported (127). For methanol, for example, the equation may be written

$$-\mathrm{d}[\mathrm{N_2O_4}]/\mathrm{d}t = k \cdot P_{\mathrm{N_2O_4}} P_{\mathrm{ROH}}$$

In systems at constant pressure the rate of reaction measured diminishes with increasing temperature between 0° and 25°C. because of the diminishing concentration of dinitrogen tetroxide. Thus the activation energy for esterification is small, probably near 5 kcal. mole^{-1}. (For other references see 274 and 354.)

3. The heterogeneous reaction

The careful work of Fairlie, Carberry, and Treacy (127) has revealed the occurrence of a heterogeneous reaction between alcohols and dinitrogen tetroxide which is assisted by a polar surface (213). Thus, practically no reaction is observed on paraffin wax surfaces under conditions leading to considerable rates on glass, aluminum, and Teflon vessels. The addition of nitric acid also had a marked effect in increasing the initial reaction rate. It is suggested that the alcohol is the strongly adsorbed species (213).

4. Reaction in the presence of nitric oxide

Esters of nitrous acid from the reaction of alcohols with "nitrous fumes" were reported over fifty years ago (139, 372); however, because the temperatures were not kept low, concurrent oxidation obscured the reactions. When the temperature is not allowed to rise enough for oxidation to occur it is found that no nitric acid is formed but only the nitrous ester. Stoichiometrically:

$$\mathrm{ROH} + \mathrm{N_2O_3} \rightarrow \mathrm{RONO} + \mathrm{HONO}$$

$$\mathrm{ROH} + \mathrm{HONO} \rightarrow \mathrm{RONO} + \mathrm{H_2O}$$

Experiments with O^{18}-labelled *tert*-butyl alcohol show that again the carbon–oxygen bond is not broken in esterification (347). The reaction proceeds as indicated below:

$$\mathrm{(CH_3)_3CO^{18}H} + \mathrm{HONO_2} \rightarrow \mathrm{(CH_3)_3CO^{18}NO} + \mathrm{HONO}$$

$$\mathrm{(CH_3)_3CO^{18}H} + \mathrm{HONO} \rightarrow \mathrm{(CH_3)_3CO^{18}NO} + \mathrm{H_2O}$$

The simplest explanation of reaction is that, as with water, dinitrogen trioxide reacts faster with alcohols than does dinitrogen tetroxide, although this view has been challenged (127).

When oxygen is bubbled through the alcohol–dinitrogen trioxide system the corresponding nitrate is produced (422).

5. The reaction of dinitrogen tetroxide with ketones

At room temperature, and in either the liquid or the gas phase, acetone reacts with dinitrogen tetroxide, giving a complex series of products (437). Among the products found are nitro compounds and nitrate esters, and hydrogen cyanide is liberated from acidified solutions.

At 160°C. no reaction occurs, according to Levy (230); by 400°C. reactions of hydrogen abstraction and nitration by nitrogen dioxide set in. Thus the low-temperature reaction must be ascribed to dinitrogen tetroxide; the ketone probably reacts in the enol form. At temperatures above 160°C. dinitrogen tetroxide is absent and tendencies to $\mathrm{NO^+NO_3^-}$ have vanished with it.

Ethyl methyl ketone also reacts with dinitrogen tetroxide, but less rapidly than acetone (347).

From benzyl phenyl ketone the oxime has been isolated (336).

D. THE REACTION OF DINITROGEN TETROXIDE WITH AMMONIA AND AMINES

The members of the nitrogen series NH_3, RNH_2, R_2NH, and R_3N parallel those of the oxygen series OH_2, ROH, R_2O, and so do their reactions with dinitrogen tetroxide. Thus both tertiary amines and ethers form compounds; both secondary amines and alcohols give nitroso derivatives—nitrosoamines and alkyl nitrites. Just as with water, reaction with ammonia leads to considerable decomposition, which is the more extensive because the possibilities of forming the extraordinarily stable molecular nitrogen make it more exothermic. Primary aliphatic and aromatic amines are both supposed to undergo nitrosation, although only as a preliminary to further reaction—deamination and diazotization, respectively. Once again it seems that all the observed reactions are illuminated by the concept of dinitrogen tetroxide ionizing to NO^+ and NO_3^-.

Ammonium salts and substituted ammonium salts react by virtue of their hydrolysis to ammonia or amines or by their possession of a reactive anion (see Section IX,F).

1. Ammonia

Even with solid dinitrogen tetroxide ammonia reacts readily and extensively; because of the secondary exothermic reactions decomposition is very complete. A controlled reaction leads to the formation of water, nitric oxide, nitrogen, and ammonium nitrate (53, 128, 310) and some nitrous oxide and ammonium nitrite. Ammonium nitrate has been manufactured from ammonia, water vapor, nitrous fumes, and oxygen (297).

The gas-phase reaction between ammonia and nitrogen dioxide has been investigated between 150° and 200°C. (128). The overall equation is given as:

$$2NO_2 + 2NH_3 \rightarrow NH_4NO_3 + N_2 + H_2O$$

From pressure–time curves the reaction was found to be of third order: first order with respect to ammonia and second order with respect to nitrogen dioxide. It was found that the specific third-order rate constant decreased with temperature, for which the energy of activation was -12.5 kcal. From these results it has been proposed that dinitrogen tetroxide and not nitrogen dioxide is the active species in the reaction.

2. Primary amines

In acid solution dinitrogen tetroxide and nitrous acid are both excellent nitrosating agents. Kinetic data are available (388, 389) for deamination by nitrous acid of aliphatic primary amines which show dinitrogen trioxide to be the active agent; in the dinitrogen tetroxide reaction it is probably this substance (N_2O_4) itself.

Identical kinetics govern the diazotization of aromatic amines (357).

3. Secondary amines

Again, kinetic data for nitrosation by nitrous acid are available (201). These indicate (201) dinitrogen trioxide as the active species in nitrous acid nitrosation, and dinitrogen tetroxide in this system:

$$R_2NH + \overset{\delta+}{NO}\,\overset{\delta-}{NO_3} \rightarrow R_2NNO + H^+ + NO_3^-$$

Work has recently been done on the formation of diethylnitrosoamine in the reaction of diethylammonium chloride and dinitrogen tetroxide (8). In this system simultaneous reaction with the chloride anion produces nitrosyl chloride; the diethylnitrosoamine also forms an addition complex with dinitrogen tetroxide which is formulated as $[(C_2H_5)_2(NO)N]_2NO^+NO_3^-$.

E. THE REACTION OF DINITROGEN TETROXIDE WITH METALS

1. Reaction at low temperatures

Metals whose reactions with dinitrogen tetroxide have been noted are given in standard works on inorganic chemistry (156, 258). One clear generalization emerges: all metals which react at low temperatures are converted into nitrates and liberate nitric oxide.

$$M + N_2O_4 \rightarrow MNO_3 + NO$$

Reaction may be described as the transfer of an electron from the metal to the dinitrogen tetroxide molecule, yielding the metal ion–nitrate ion pair in place of $NO^+NO_3^-$; the nitric oxide is liberated. Reaction may end here if the metal is very electropositive and the temperature low. However, further amphoteric reaction with dinitrogen tetroxide may lead to the metal in the anion of a nitrosonium salt.

At elevated temperatures decomposition of the nitrate to oxide or nitrite occurs; no nitrite is ever formed directly. This is the course of reaction with, for example, sodium (28, 199, 344), potassium, zinc (15, 21, 23), silver (115, 293), and lead (344). It is the reaction which occurs when nitrogen dioxide attacks the surface in a mercury manometer to form mercurous and mercuric nitrates (15, 21, 23, 115, 293). Addison's (15, 21, 23) work on the reaction of zinc with dinitrogen tetroxide is the best investigated; as it is typical of metal reactions its salient features will be outlined here.

Reaction of zinc with pure dinitrogen tetroxide: At first, nitric oxide is evolved and zinc nitrate is formed. As reaction proceeds, an insoluble compound of the empirical formula $Zn(NO_3)_2 \cdot 2N_2O_4$ is deposited. This is a nitrosonium salt with

$$Zn + 2N_2O_4 \rightarrow Zn(NO_3)_2 + 2NO\uparrow$$

$$Zn(NO_3)_2 + 2N_2O_4 \rightleftharpoons (NO)_2Zn(NO_3)_4$$

the tetranitrozincate anion. This anion is analogous to the ions $Zn(OH)_4^{2-}$ and $Zn(NH_2)_4^{2-}$ in the water and ammonia systems. The complex salt formed as a result of this amphoteric behavior decomposes at 100°C. into dinitrogen tetroxide and pure anhydrous zinc nitrate.

The activation energy for the dissolution of zinc in dinitrogen tetroxide has been measured. Between -11.2°C. and $+14$°C. the Arrhenius activation energy is $\sim$ 4500 cal. mole^{-1} (15). The dissolution of zinc or magnesium in dilute aqueous hydrochloric acid gives $E \sim$ 4230 and 5000, respectively, and is believed to be controlled by electron transfer at the metal–solution interface; the same explanation is offered here, the active species in dinitrogen tetroxide being assumed to be the ion-pair $NO^+NO_3^-$.

Solution of zinc in mixtures of dinitrogen tetroxide with dinitrogen trioxide, nitrosyl chloride, and diethylnitrosoamine: When dinitrogen trioxide is present (0–40 per cent), reaction proceeds faster (22); at 0°C. the rate is eight times as great in a mixture containing 40 per cent dinitrogen trioxide as in pure dinitrogen tetroxide. The product is the same. Two factors have been suggested to explain the change in rate: (*1*) An increase in dielectric constant with added dinitrogen trioxide which yields a higher concentration of $NO^+NO_3^-$ ion-pairs. Certainly the electrical conductivity is enhanced by added dinitrogen trioxide. (*2*) Displacement of the equilibria existing in liquid dinitrogen tetroxide so as to favor NO^+. Quantitatively the rate has been represented as $\propto [N_2O_3]^{1/2}$; in a medium of altering dielectric constant it is impossible to translate this into ionic concentrations.

When nitrosyl chloride is present (16), the reaction rate is again increased. Over the major portion of the concentration range 0–40 per cent nitrosyl chloride, the rate of reaction is proportional to $[NOCl]^2$; in a solution 8 molar in nitrosyl chloride the rate of solution is five times greater than in pure dinitrogen tetroxide. (This molarity of dinitrogen trioxide produces an eightfold increase.) A new product appears in addition to the complex nitrate—a complex chloride having the empirical formula $ZnCl_2NOCl$. The reactions occurring in these mixtures have been summarized as follows:

(a) $$Zn + 2N_2O_4 \rightarrow Zn(NO_3)_2 + 2NO$$

$$Zn(NO_3)_2 + 2N_2O_4 \rightarrow (NO)_2Zn(NO_3)_4$$

(b) $$Zn + 2NOCl \rightarrow ZnCl_2 + 2NO$$

$$2ZnCl_2 + 2NOCl \rightarrow (NO)_2Zn_2Cl_6$$

Nitrate and chloride are interchangeable to some extent in the complex anions (16).

When diethylnitrosoamine is present, zinc dissolves to yield the same complex nitrate anion but associated with the coördinated nitrosonium cation. Stoichiometrically:

$$Zn + 4N_2O_4 + 4(C_2H_5)_2NNO \rightarrow [[(C_2H_5)_2NNO]_2NO^+]_2[Zn(NO_3)_4^{2-}] + 2NO$$

Zinc has also been dissolved in solutions of substituted ammonium nitrates in dinitrogen tetroxide. Still the same tetranitrozincate anion is formed finally, but this time the appropriate substituted ammonium group competes with NO^+ as cation (14).

2. Reaction at high temperatures

At high temperatures metals react to yield a mixture of products, many of which may be derived from decomposition of nitrate formed initially in the manner described, but some of which are more likely the result of oxidation by nitrogen dioxide. Thus, potassium burns with a red flame, forming nitrite as well as nitrate (115, 293); magnesium is oxidized at dull-red heat (344); and manganese, iron, cobalt, and nickel are oxidized (344). The increased rate of reaction of zinc with dinitrogen tetroxide above 14°C. has been ascribed to the onset of reaction between nitrogen dioxide and zinc to form zinc oxide, followed by rapid solution of the oxide (15).

F. THE REACTION OF DINITROGEN TETROXIDE WITH ANIONS

Liquid and gaseous dinitrogen tetroxide react readily with many salts. The cation M^+ is often unaltered, and the anion X^- is the reactive species. These reactions may be generalized as electron transfer from anion to dinitrogen tetroxide to yield nitric oxide and the nitrate anion.

$$N_2O_4 + X^- \rightarrow NO + NO_3^- + X$$

The discharged anion X may itself be a very reactive species—e.g., a chlorine atom or an azide radical—and undergo further rapid and extensive changes. When reaction occurs between dinitrogen tetroxide and solid MX, although M may appear not to enter into reaction as written above, it exercises a strong effect through the dependence on M^+ of the lattice energies of MX and MNO_3 and hence of the free-energy change of reaction.

When the anion is the anion of an oxy acid, HOY, another description of the same process is displacement of one acid anhydride by another:

$$2MOY + 2N_2O_4 \rightarrow 2MNO_3 + Y_2O + N_2O_3(NO + NO_2)$$

This type of reaction includes reaction with, for example, the alkali metal hydroxides, for on the $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$ acid-base system water no less than acetic anhydride or carbon dioxide deserves the name "acid anhydride." In agreement with these general principles, the nitrate anion is unaffected by dinitrogen tetroxide.

The reactions following are examples of this behavior. Further instances are listed in standard texts (156).

1. Salts of monobasic acids not containing oxygen: chlorides, bromides, iodides, and azides

Chlorides: Ionic chlorides undergo reaction with dinitrogen tetroxide to yield the nitrate and nitrosyl chloride: the one which has been most thoroughly investigated is potassium chloride (44, 256, 332a, 421); others include ammonium chloride (53), diethylammonium chloride (24), calcium chloride, zinc chloride, titanium tetrachloride, and stannic chloride (156).

Potassium nitrate has been manufactured on an industrial scale from the reaction between moist potassium chloride crystals and dinitrogen tetroxide at ordinary temperatures (44, 256, 332a, 421).

$$\mathrm{KCl(s)} + \mathrm{N_2O_4(g)} \rightarrow \mathrm{KNO_3(s)} + \mathrm{NOCl(g)}$$

$$\Delta F^0_{298.1} = -4496 \text{ cal.}; \Delta H^0_{291.1} = -3683 \text{ cal.}$$

Bromides: Bromides behave similarly, reacting with dry dinitrogen tetroxide to form bromine, nitric oxide, and the solid nitrate (156).

$$\mathrm{KBr} + \mathrm{N_2O_4} \rightarrow \mathrm{KNO_3} + \mathrm{NO} + \tfrac{1}{2}\mathrm{Br_2}$$

Iodides: Iodides undergo a set of reactions influenced by the conditions (365). Both solid potassium iodide and methylammonium iodide (as solid or in nitromethane solution) react according to the equation:

$$\mathrm{MI} + \mathrm{N_2O_4} \rightarrow \mathrm{MNO_3} + \mathrm{NO} + \tfrac{1}{2}\mathrm{I_2}$$

In aqueous solution, nitrate and nitrite may both be formed according to the equations (365):

$$\mathrm{N_2O_4} + 2\mathrm{I^-} \rightarrow 2\mathrm{NO_2^-} + \mathrm{I_2} \qquad (1)$$

$$\mathrm{N_2O_4} + \mathrm{I^-} \rightarrow \mathrm{NO_3^-} + \mathrm{NO} + \tfrac{1}{2}\mathrm{I_2} \qquad (2)$$

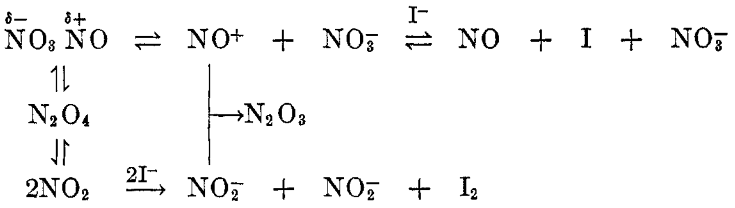
Reactions 1 and 2 are faster than the reaction of dinitrogen tetroxide with water. Since both iodine and dinitrogen tetroxide can oxidize nitrites to nitrates (Section 9,F,1), reaction 2 may be regarded as an extension of reaction 1 brought about either by reaction 1a, which occurs when the mole ratio $\mathrm{I^-/N_2O_4}$ is less than unity:

$$\mathrm{NO_2^-} + \mathrm{N_2O_4} \rightarrow \mathrm{NO_2}(\tfrac{1}{2}\mathrm{N_2O_4}) + \mathrm{NO} + \mathrm{NO_3^-} \qquad (1a)$$

or by reaction 1b when $\mathrm{I^-/N_2O_4}$ is greater than unity:

$$\mathrm{NO_2^-} + \mathrm{I_2} \rightarrow \mathrm{NO_2}(\tfrac{1}{2}\mathrm{N_2O_4}) + \mathrm{I}(\tfrac{1}{2}\mathrm{I_2}) + \mathrm{I^-} \qquad (2a)$$

Seel interprets the reaction in terms of electron transfer from iodide ion (*1*) to dinitrogen tetroxide, forming NO and $\mathrm{NO_3^-}$, and (*2*) to monomeric nitrogen dioxide, forming $\mathrm{NO_2^-}$.



$$\begin{tikzcd}
\overset{\delta-}{\mathrm{NO_3}}\,\overset{\delta+}{\mathrm{NO}} \arrow[r, shift left] \arrow[d, shift left] & \mathrm{NO^+} + \mathrm{NO_3^-} \arrow[l, shift left] \arrow[r, shift left, "\mathrm{I^-}"] \arrow[d] & \mathrm{NO} + \mathrm{I} + \mathrm{NO_3^-} \arrow[l, shift left] \\
\mathrm{N_2O_4} \arrow[u, shift left] \arrow[d, shift left] & \mathrm{N_2O_3} & \\
2\mathrm{NO_2} \arrow[u, shift left] \arrow[r, "2\mathrm{I^-}"] & \mathrm{NO_2^-} + \mathrm{NO_2^-} + \mathrm{I_2} \arrow[u] &
\end{tikzcd}$$

The possible existence of nitrosyl iodide as an intermediate has been discussed (362).

Azides: Very similar reactions occur between dinitrogen tetroxide and the azides. Tetramethylammonium azide in excess dinitrogen tetroxide, or in nitromethane as solvent, and aqueous sodium azide react according to the equation:

$$N_3^- + N_2O_4 \rightarrow NO_3^- + N_2 + N_2O$$

The compound ON_4 ($NO + N_3$) may be formed as an intermediate (363); clearly such an intermediate must occur during reaction.

These separate studies on reactions with azide and iodide have enabled Seel to elucidate in similar terms the reaction between nitrites and azides in the presence of iodine.

2. Salts of monobasic oxy acids and anions containing oxygen: fatty acids, nitrites, hydroxides, chlorates

Sodium acetate, sodium propionate, sodium butyrate: Good yields of acetic, propionic, and butyric anhydrides have been obtained by heating the dry sodium salts of the corresponding acids with dinitrogen tetroxide.

$$2CH_3COONa + 2N_2O_4 \rightarrow (CH_3CO)_2O + 2NaNO_3 + N_2O_3$$

This reaction may be regarded as mediated by the hypothetical mixed anhydride $CH_3CO \cdot O \cdot NO$.

Nitrites: The reaction between the aqueous nitrite ion and dinitrogen tetroxide has been mentioned in the previous section. In the solid state the same reaction occurs; sodium, calcium and silver nitrites are all oxidized to the corresponding nitrates and nitric oxide is liberated (293, 299).

Hydroxides: In aqueous solution hydroxide ions are replaced by nitrite and nitrate ions as reaction with dinitrogen tetroxide proceeds. However, the evidence is clear that nitrite-ion formation is only a secondary step following the production of NO_3^-, H^+, and HONO. Classically (122, 156, 173, 221) the same reaction has been written for the solid sodium potassium and barium hydroxides:

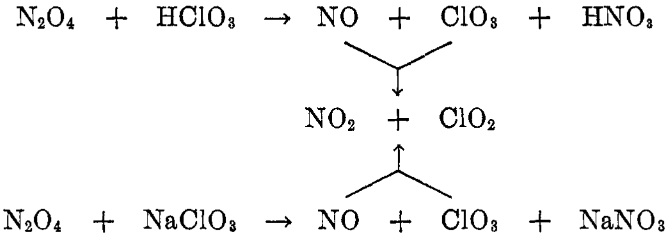
$$2NaOH + N_2O_4 \rightarrow NaNO_3 + NaNO_2 + H_2O$$

although the possibility of oxidation of nitrite by excess dinitrogen tetroxide has been recognized. Recently it has been reported that when dry sodium hydroxide (obtained by heating for 3 hr. at 320°C. in a silver vessel in a stream of oxygen) reacts vigorously with liquid dinitrogen tetroxide (18) only 2.5 per cent sodium nitrite forms under conditions yielding 94 per cent conversion to sodium nitrate.

$$Na^+OH^- + NO^+NO_3^- \rightarrow Na^+NO_3^- + HONO$$

This result may not exclude initial formation of both nitrite and nitrate, however, followed by oxidation of the nitrite. The conclusion, drawn by Addison (18), that "the nitrous acid molecule reacts only slightly with sodium hydroxide" is not an attractive one.

Chlorates: Recent work has shown that when nitrogen dioxide is passed over moist sodium chlorate (282) or sodium chlorate containing nitric acid (391) chlorine dioxide is formed in good yield. It is possible that the chlorine dioxide comes from reaction between $NO + ClO_3$ formed from such reactions as the following:



3. Divalent anions: carbonates, dibasic fatty acid salts, oxides, sulfites, and sulfates

Carbonates: Sodium carbonate dried at 600°C. reacts very slowly with liquid dinitrogen tetroxide. After 24 hr., when 14.6 per cent conversion of sodium carbonate has taken place, only sodium nitrate is formed (18):

$$Na_2CO_3 + 2N_2O_4 \rightarrow 2NaNO_3 + CO_2 + N_2O_3$$

Reaction at higher temperatures is more rapid and oxidation by nitrogen dioxide occurs. At 250°C. reaction for 7 hr. produced 33 per cent conversion. The equation written for this reaction (18) is formally the same as that above, with N_2O_4 and N_2O_3 replaced by $2NO_2$ and $NO_2 + NO$, respectively; both equations represent replacement of one acid anhydride by another. No nitrite is formed at any temperature. The same reaction is reported (67a) for calcium carbonate.

Succinates; phthalates: Riebsomer and Reinecke (337) report a 75 per cent yield of the cyclic acid anhydrides from the sodium salts when treated with dinitrogen tetroxide.

Oxides: Calcium and zinc oxides react with liquid dinitrogen tetroxide, forming the metal nitrate only; no nitrites are produced (19a). The equations written are of the general form:

$$CaO + 2N_2O_4 \rightarrow Ca(NO_3)_2 + N_2O_3$$

In the gas-phase reaction, at temperatures up to 140°C., the products are the same. Above 140°C., however, reactions are much more rapid and some nitrite is formed as well as nitrate. The amount of nitrite formed decreases with increased temperature and reaction time. Other reactions studied include reaction with barium oxide, soda lime and potash lime, and cuprous oxide (156).

Higher oxides: Sodium peroxide forms sodium nitrate at temperatures below 140°C. and some nitrite at temperatures above this (19a). Lead dioxide absorbs nitrogen dioxide quantitatively to form lead nitrate (111a).

Sulfites and sulfates: Seel and Meier (362a) in the course of experiments on the reactions of the lead chamber process investigated some of the reactions of sulfites, sulfates, and fluorosulfinates with dinitrogen tetroxide. They used liquid sulfur dioxide as solvent. The reactions discovered were essentially the same as those of other nitrosyl compounds; e.g., NOCl, $NOBF_4$. The gaseous products found included nitric oxide, nitrous oxide, and nitrogen.

They indicate the relative proportions of different reactions as follows:

1. With sulfites:

$$N_2O_4 + 4SO_3^{2-} \rightarrow N_2 + 4SO_4^{2-} \qquad \sim 3 \text{ per cent}$$

$$N_2O_4 + 3SO_3^{2-} \rightarrow N_2O + 3SO_4^{2-} \qquad \sim 45 \text{ per cent}$$

$$N_2O_4 + 2SO_3^{2-} \rightarrow 2NO + 2SO_4^{2-} \qquad \sim 16 \text{ per cent}$$

$$N_2O_4 + SO_4^{2-} \rightarrow 2NO_3^- + SO_2 \qquad \sim 10 \text{ per cent}$$

$$N_2O_4 + 2SO_3^{2-} + 2SO_2 \rightarrow 2[NO(SO_3)_2^{2-}] \qquad \sim 16 \text{ per cent}$$

2. With sulfates:

$$N_2O_4 + 4SO_4^{2-} + 4SO_2 \rightarrow N_2 + 4S_2O_7^{2-} \qquad \sim 55 \text{ per cent}$$

$$N_2O_4 + 3SO_4^{2-} + 3SO_2 \rightarrow N_2O + 3S_2O_7^{2-} \qquad \sim 8 \text{ per cent}$$

$$N_2O_4 + 2SO_4^{2-} + 2SO_2 \rightarrow 2NO + 2S_2O_7^{2-} \qquad \sim 3 \text{ per cent}$$

$$N_2O_4 + SO_4^{2-} \rightarrow 2NO_3^- + SO_2 \qquad \sim 34 \text{ per cent}$$

The reaction involving $N_2O_4 + SO_2 + SO_4^{2-}$ may form N_2O_3 as an intermediate product.

3. With fluorosulfinates:

$$N_2O_4 + 4SO_2F^- \rightarrow N_2 + 4SO_3F \qquad \sim 20 \text{ per cent}$$

$$N_2O_4 + 3SO_2F^- \rightarrow N_2O + 3SO_3F \qquad \sim 35 \text{ per cent}$$

$$N_2O_4 + 2SO_2F^- \rightarrow 2NO + 2SO_3F \qquad \sim 2 \text{ per cent}$$

Mechanisms for these reactions involving both NO^+ and NO_2 have been proposed (362a).

X. REACTIONS OF THE NITRONIUM ION, NO_2^+

In Section IV the structure of NO_2^+ was discussed and a number of its crystalline derivatives listed. The nitronium ion is also important in numerous solutions in sulfuric acid, as is indicated by spectroscopic and cryoscopic data and by chemical reactivity. Typical of this reactivity is its nitrating power, and if nitrating solutes of the formula XNO_2 are arranged in order of increasing nitrating power (153), then

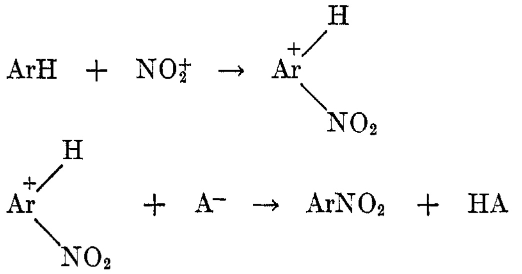
$$\begin{array}{lccccccc} XNO_2 = & C_2H_5ONO_2 & < HONO_2 & < CH_3COONO_2 & < NO_3NO_2 & < ClNO_2 & < H_2ONO_2^+ & < NO_2^+ \\ HX = & C_2H_5OH & H_2O & HOCOCH_3 & HNO_3 & HCl & H_3O^+ & H^+ \end{array}$$

This order is also the order of increasing strengths of the acids HX. A plot giving the concentration of NO_2^+ in solutions of nitric acid and sulfuric acid may be found in the review by Gillespie and Millen (153).

A. NITRATION IN ACID MEDIA BY NO_2^+

1. *The nitration step*

The following scheme (203) has been outlined for electrophilic substitution by NO_2^+ in aromatic compounds of the general formula ArH:



Slow, second order

Fast

Uptake of the nitronium ion is slow compared with the subsequent proton transfer. In this scheme HA is the strongest acid present—e.g., sulfuric acid in the HNO_3–H_2SO_4 mixed acids.

2. *Nitration inhibited by nitrous acid or dinitrogen tetroxide*

Nitrous acid retards nitration in nitric acid, nitromethane, and acetic–nitric acid mixtures (200). In nitric acid solution, nitrous acid exists essentially in the same form as dinitrogen tetroxide, i.e., a mixture of nitrosonium and nitrate ions (160):

$$HONO + HNO_3 \rightarrow NO^+ + NO_3^- + H_2O$$

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

These nitrate ions of course displace the ionization equilibria involving NO_2^+ so as to reduce the formation of nitric acidium ions ($H_2NO_3^+$)

$$2HNO_3 \rightarrow H_2NO_3^+ + NO_3^-$$

$$H_2NO_3^+ \rightarrow NO_2^+ + H_2O$$

and hence NO_2^+. Since the concentration of NO_2^+ is lowered, so is the rate of direct nitration.

A still stronger inhibition occurs with increased amounts of water and of nitrous acid or dinitrogen tetroxide when nitrite ion is produced. This is of course a much stronger base than nitrate ion and much more effective in deprotonating the nitric acidium ion.

3. *Nitration catalyzed by nitrous acid or dinitrogen tetroxide*

Catalysis by nitrous acid and by nitrogen dioxide of nitrations of aromatic compounds containing OR and NR_2 substituents has also been observed (56, 203). These compounds are highly reactive to electrophilic attack, whether by

NO^+ or by NO_2^+. Although the presence of nitrous acid reduces the concentration of NO_2^+, the NO^+ ions present (N_2O_4 is a weak electrolyte: $K_A \sim 2 \times 10^{-3}$ in acetic acid–nitric acid mixtures) rapidly nitrosate the aromatic compound

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

ArH to ArNO. Even more rapid oxidation of the nitroso derivative, ArNO, to the nitro compound, $ArNO_2$, follows. Thus, although NO^+ is specifically less reactive than NO_2^+, the concentration of NO_2^+ is so reduced in these circumstances that direct nitrosation is more rapid than direct nitration. As nitrosation is followed by speedy oxidation, the overall nitration rate is increased.

B. ESTERIFICATION BY THE NITRONIUM ION, NO_2^+

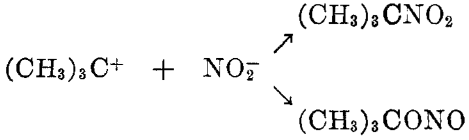
Nitrate esters may be prepared from alcohols and the nitronium ion. As in nitrations, all acid anhydrides (of the general formula XNO_2) which will yield NO_2^+ are satisfactory. Thus, dinitrogen pentoxide with ethanol and *tert*-butyl alcohol yields the nitrate ester (347), as does nitryl fluoride (NO_2F) with ethanol (196). The part played by NO_2^+ in the esterification of alcohols by the mixed acids sulfuric and nitric acid and by nitric acid alone still requires clarification.

XI. REACTIONS OF THE NITRITE ION

In the solid state relatively few simple nitrites are known. The nitrite ion has a pronounced tendency to form coördination compounds. In solution the nitrite ion is found in aqueous systems containing alkali and alkaline earth nitrites, i.e., solutions with pH > 7. The acid ionization constant of nitrous acid (K_A mole liter^{-1}) is only 6×10^{-4} at 30°C., and thus many of the reactions of the nitrite ion in acid media are reactions of nitrous acid. For these and for the numerous organic reactions of nitrous acid the reader is referred to standard texts on inorganic and organic chemistry.

A. REACTION OF THE NITRITE ION, NO_2^-, WITH THE CARBONIUM ION

When alkyl halides, particularly the iodides, are treated with silver nitrite, nitroparaffins and alkyl nitrites are formed. When potassium nitrite is used, the tendency to form the alkyl nitrite is greater (371). The reaction between *tert*-butyl bromide and tetramethyl(or ethyl)ammonium nitrite in nitromethane solution has recently been investigated (254). The reactions are both first order with respect to halide and zero order in nitrite ion; the rate-determining step is the ionization of the alkyl halide to the carbonium ion. This reacts with the nitrite ion to yield both 2-methyl-2-nitropropane and *tert*-butyl nitrite,



$$(CH_3)_3C^+ + NO_2^- \begin{array}{l} \nearrow (CH_3)_3CNO_2 \\ \searrow (CH_3)_3CONO \end{array}$$

demonstrating that both the oxygen and the nitrogen of NO_2^- are centers for electrophilic attack. In addition to these reactions, elimination occurs as well, with the formation of isobutylene. (See also reference 222a.)

B. REACTIONS OF THE NITRITE ION, NO_2^-, IN ALKALINE MEDIA

Even weak oxidizing agents, e.g., atmospheric oxygen, convert nitrites to nitrates in alkaline media. Some of the more important oxidation–reduction potentials (265) are:

$$\begin{array}{lr} & E^0_{298} \\ NO_2^- + 2OH^- \rightleftharpoons NO_3^- + H_2O + 2e & -0.01 \text{ v.} \\ NO + 2OH^- \rightleftharpoons NO_2^- + H_2O + e & +0.46 \text{ v.} \\ N_2O + 6OH^- \rightleftharpoons 2NO_2^- + 3H_2O + 4e & -0.15 \text{ v.} \end{array}$$

C. REACTIONS OF NITRITES IN ACID MEDIA

In acid media, nitrites exist as nitrous acid ($K_A \sim 6 \times 10^{-4}$). Some of the appropriate oxidation–reduction potentials in acid media are:

$$\begin{array}{lr} & E^0_{298} \\ N_2O + 3H_2O \rightleftharpoons 2HNO_2 + 4H^+ + 4e & -1.29 \text{ v.} \\ NO + H_2O \rightleftharpoons HNO_2 + H^+ + e & -0.99 \text{ v.} \\ HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + e & -0.94 \text{ v.} \end{array}$$

A sensitive test for nitrous acid is its reaction with a solution of sulfanilic acid and α-napthylamine in acetic acid (Griess reagent). The azo dye formed is pink, and its concentration may be determined colorimetrically for the quantitative estimation of nitrous acid.

Esterification of alcohols, nitrosation of amines and phenols, and diazotization of amines are among the many reactions with organic compounds undergone by nitrous acid; an excellent introduction to these organic reactions is given by Sidgwick (371). Accounts of the inorganic reactions are to be found in Gmelin's *Handbuch* (156) and many recent texts (265).

XII. OTHER DERIVATIVES: REACTIONS OF THE IONS NO_2^{2-} AND $N_2O_4^{2-}$

A. THE HYDRONITRITE ION, NO_2^{2-}

When a solution of sodium nitrite in liquid ammonia is reduced with sodium a bright yellow solid is precipitated; its formula is Na_2NO_2 (255, 440). Virtually nothing detailed is known either of its chemistry or of its structure. It explodes in moist air and hydrogen is formed. With oxygen it reacts to form a peroxide. When protected from moisture and oxygen, the dry salt may be heated to 100°C. without decomposition, but above this temperature violent decomposition takes place to sodium oxide, sodium nitrite, sodium nitrate, and nitrogen.

B. THE ION $N_2O_4^{2-}$

When sodium hyponitrite, $Na_2N_2O_2$, is oxidized with liquid dinitrogen tetroxide, the compounds $Na_2N_2O_3$ and $Na_2N_2O_4$ are formed (10). Little is known of their chemistry. With water, $Na_2N_2O_4$ reacts to evolve nitrous oxide.

XIII. ANALOGOUS SYSTEMS

A. NITROSYL CHLORIDE

Though the nitrogen dioxide–dinitrogen tetroxide system shows an extraordinary diversity of chemical properties, the preceding sections illustrate how a limited number of basic principles are able to provide a sound basis for interpretation. The question arises: is this system unique or are there close analogs? The answer depends on how strict our requirements are. Useful comparisons can be made with systems that do not share all the properties of nitrogen dioxide. Thus the behavior of nitrosyl chloride (44) shows many similarities, although it does not share any of the free-radical properties. Its behavior as an ionizing solvent is based on NO^+ and Cl^- instead of NO^+ and NO_3^- (76, 238). Thus, with silver perchlorate it yields silver chloride and nitrosyl perchlorate; with silver nitrate, nitrogen dioxide (298, 307). Hydrolysis or alcoholysis yields hydrochloric acid and (respectively) nitrous acid or an alkyl nitrite (226, 356). In addition to unsaturated compounds on the other hand, primary homolysis to NO and Cl offers as adequate an explanation as does primary homolysis to $2NO_2$ by N_2O_4.

B. OTHER OXIDES OF NITROGEN

The other oxides of nitrogen offer further parallels. Nitric oxide dimerizes to $(NO)_2$ and shares many free-radical properties with nitrogen dioxide. On the other hand, its role as the mixed acid anhydride of HNO_2 and "HNO" is virtually non-existent, although sodium and potassium nitrosyls have been claimed. However, its compound with nitrogen dioxide is nitrous anhydride, now well characterized and the basis of all nitrites. With nitrogen trioxide (NO_3), it yields nitrogen dioxide, of course.

Dinitrogen pentoxide forms a solid which is actually ionic ($NO_2^+NO_3^-$) and thus has the same relation to N_2O_4 as NO_2^+ has to NO^+. Although the nitrate radical NO_3 is now well known, its dimer, N_2O_6, is less well substantiated. This, the mixed anhydride of nitric and pernitric acids, may be $NO_2^+NO_4^-$, where NO_4^- contains the peroxy group and is O—O—NO_2 (133).

C. OXIDES OF OTHER GROUP VA ELEMENTS

Phosphorus, arsenic, and antimony all form oxides of the empirical formula XO_2. The phosphorus derivative, usually written P_2O_4, yields with water a mixture of phosphorous acid, H_3PO_3, and phosphoric acid, H_3PO_4; vapor density measurements suggest that, far from dissociating readily in the gas phase, it is present as P_8O_{16} (418). Antimony tetroxide has been represented formally as $Sb^{III}Sb^{V}O_4$, but this formula is not structurally satisfactory as it does not agree with x-ray work; the formula $SbO^+ \cdot SbO_3^-$ may represent its properties better.

D. HALOGEN ANALOGS

Some of the most striking analogies are with halogen derivatives. The chemistry of the halogen oxides has recently been illuminated by some excellent European work and there is no doubt that the dinitrogen tetroxide system, which has been studied in much more detail, will prove a very valuable reference in the systemization of the halogen oxide derivatives (227).

Two types of analogs may be chosen. On structural grounds derivatives of the type ClO_2, (Cl_2O_4) and (IO_2), I_2O_4 are the obvious choices. It has also been argued (227) that since nitrogen belongs to Group V and the halogens to Group VII, in choosing similar systems N^{III} should be replaced by Cl^{V}, etc.

1. "Structurally" analogous halogen oxides

Chlorine dioxide and nitrogen dioxide, both of which are angular, odd-electron molecules, dimerize to mixed acid anhydrides, X_2O_4. With potassium hydroxide Cl_2O_4 yields chlorite and chlorate anions.

"Chlorosonium" derivatives of ClO^+ (analogous to NO^+) have been discussed (432).

The oxide I_2O_4 is considered as $IO(IO_3)$, and similar derivatives of IO, such as $IO_2(SO_4)$, are also known (67). The reactions of IO^+ and IO_2^+ with aromatic compounds resemble those of NO^+ and NO_2^+.

2. "Chemically" analogous halogen oxides

On the basis of replacing derivatives of N^{III} and N^{V} by Cl^{V} and Cl^{VII} the following pairs of compounds may be derived for comparison:

NO	ClO_2	$(NO)_2$	Cl_2O_4
NO^+	ClO_2^+		
NO^-	ClO_2^-		
		N_2O_3	Cl_2O_5
NO_2	ClO_3	N_2O_4	Cl_2O_6
NO_2^+	ClO_3^+		
NO_2^-	ClO_3^-		
		N_2O_5	Cl_2O_7
NO_3	ClO_4		
NO_3^-	ClO_4^-		

Then the equation

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

is replaced by

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

So far the flow of information about the systems is largely one-way, but as the chemistry of the chlorine oxides is extended, they may be expected to improve our knowledge of the nitrogen system.

E. STRUCTURALLY ANALOGOUS SYSTEMS

Structurally, the isoelectronic principle is the guide in the search for comparison compounds. This is very valuable in interpreting the relations in the series NO_2^+, NO_2, NO_2^-, and NO_2^{2-}. Thus parallels to NO_2^+ which share its linear structure are to be found among substances as diverse chemically as CO_2, BeF_2, and N_3^-. Nitrogen dioxide itself has the BF_2 radical and the O_3^+ and FNO^+ ions—all at present unfamiliar compounds—as its isoelectronic equivalents. Similarly the nitrite ion, NO_2^-, is isoelectronic with ozone and with nitrosyl fluoride and like them is not linear but has an interbond angle close to 115°. The hydronitrite ion, NO_2^{2-}, has the same number of electrons as the FO_2 molecule (not yet characterized) and the NF_2 radical. Chlorine dioxide, ClO_2, is a useful guide and its known structure suggests that the process of closing the interbond angle from 180° in NO_2^+ reaches its extreme in this series with NO_2^{2-}.

Isoelectronic structural analogs of N_2O_4 are B_2F_4 and the oxalate[3] ion $C_2O_4^{2-}$. Diboron tetrafluoride is not known, but the corresponding chloride, B_2Cl_4, is known (31b) and its structure has been determined. It is planar and symmetrical and has a long B—B bond. This resemblance to N_2O_4 is most marked. Possibly even more striking is the resemblance between the oxalate ion ($C_2O_4^{2-}$) and N_2O_4. This extends beyond a similar structure and similar vibration frequencies to a remarkable parallel in chemical reactions. The evolution of carbon monoxide and carbon dioxide from a solution of an oxalate in strong sulfuric acid is familiar in elementary chemistry. When the parallel reactions of N_2O_4 and $C_2O_4^{2-}$ are written down the strong resemblance is obvious:

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

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

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

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[3] The analogy emphasized here between $C_2O_4^{2-}$ and N_2O_4 serves as a reminder that ClO_2, despite its superficial affinities with NO_2, has structural differences from it. These will make themselves felt in Cl_2O_4, which is isoelectronic with P_2F_4 and $S_2O_4^{2-}$ and which, unlike N_2O_4, will not be a planar molecule. The dithionate ion, $S_2O_4^{2-}$, has been shown by Dunitz (122a) to be non-planar.

XIV. APPENDIX

Kinetic data available for the reactions of NO_2 *species*

Class of Reaction	Example	Kinetic Order	Preëxponential Factor*	Activation Energy	References
				kcal. mole^{-1}	
Radical-radical association	$2NO_2 \rightarrow N_2O_4$	2	$10^{8.7}$	0	(79)
	$Cl + NO_2 \rightarrow ClNO_2$	2 (3)	—	—	(96)
	$NO_3 + NO_2 \rightarrow N_2O_5$	2	$10^{10.3}$	1 ± 4	(208)
Addition to unsaturated compound	C_2H_4	3	$10^{8.5}$ to $10^{10.9}$	12.5 to 18	(97)
	C_3H_6	3	$10^{9.7}$	13.6	(98)
	C_2H_2	2	$10^{7.1}$	15	(393)
Hydrogen abstraction	CH_4	2	10^{6}	21	(178)
	CH_2O	2	$10^{7.1}$ to 10^{9}	15.1 to 19	(314, 394)
	CH_3CHO	2	10^{7}	13.5	(72, 249)
	$(CHO)_2$	2	$10^{8.9}$	19.8	(394)
Metathesis (I) Oxidation by NO_2	$O \rightarrow O_2$	2	—	?4	(193, 375)
	$Na \rightarrow NaO$	2	—	?2.4	(42)
	NO exchange reactions	2	—	10.5	(228)
	$O_2 \rightarrow O_3$	2	$10^{9.1}$	50.2	(209)
	$CO \rightarrow CO_2$	2	$10^{8.7}$	27.8	(101–104)
	$SO_2 \rightarrow SO_3$	2	—	24.5	(63, 202, 223)
Metathesis (II) Oxidation of NO_2	$O_3 \rightarrow O_2$	2	$10^{9.8}$	7 ± 0.6	(212)
	$F_2 \rightarrow FNO_2$	2	$10^{9.1}$	10.5	(32, 306)
	$Cl_2 \rightarrow ClNO_2$	2	—	—	(96, 287)
	$NO_3 \rightarrow NO_2$ (exchange reaction)	2	—	—	(284, 286)
Metathesis (III)	$2NO_2 \rightarrow 2NO + O_2$	2	$10^{8.9}$	25	(61, 62, 216)
Decomposition	$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$	2	$10^{9.6}$	5 ± 3	(208)

* Expressed in liter mole^{-1} sec.$^{-1}$ units: "normal" value in these units is 10^{11} to 10^{12} for bimolecular reactions and 10^{9} to 10^{10} for termolecular reactions.

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