

384. *The Liquid Dinitrogen Tetroxide Solvent System. Part XIII.* Factors related to the Mechanism of Metal-Dinitrogen Tetroxide Reactions; the Dipolar Nature of Dinitrogen Tetroxide in the Liquid State.*

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The paper considers factors having a direct bearing on the reaction mechanisms which occur in metal-liquid dinitrogen tetroxide reactions. The following two factors concern the ion-pair mechanism: (a) Apparently discordant evidence on the dipole moments of the N_2O_4 and NO_2 molecules has been correlated. Recalculations based on published data show that all experimental results may be interpreted satisfactorily if it is assumed that $\mu_{N_2O_4}$ is zero, and that μ_{NO_2} varies with temperature, although no simple explanation of this unique variation in μ_{NO_2} is available. (b) A mechanism for the formation of $[NO^+][NO_3^-]$ ion-pairs in the liquid is postulated which involves initial heterolytic dissociation into $[NO_2^+][NO_2^-]$, followed immediately by the oxidative transfer of an oxygen atom. The following factors support the mechanism involving direct metal-tetroxide reactions: (c) The products of reaction of sodium and zinc with gaseous $N_2O_4-NO_2$ mixtures at temperatures below 150° have been shown to be identical with those obtained from the liquid tetroxide. (d) Conditions are defined under which sodium nitrite is stable in contact with gaseous $N_2O_4-NO_2$ mixtures.

In previous papers in this series (*e.g.*, Part VIII, *J.*, 1951, 2833; Part IX, *J.*, 1951, 2838) kinetic measurements of the reaction between metallic zinc and liquid dinitrogen tetroxide have been interpreted on the basis of two mechanisms of reaction: the first, operative at low temperatures, involves an electron-transfer reaction between the zinc and ion-pairs of the form $[NO^+][NO_3^-]$, and the second, which predominates above 14° , involves fission of the N-N bond of the tetroxide on impact at the metal surface, followed by reaction between the metal and nitrogen dioxide. The metal oxide produced is then assumed to react directly with dinitrogen tetroxide to give the metal nitrate. Since reactions involving other metals (notably uranium) may be interpreted on the same mechanisms, it is necessary to consider the evidence upon which these reaction mechanisms are based.

There are five factors of importance to which reference has not been made previously. They concern (a) the dipole moments of the N_2O_4 and NO_2 molecules, (b) the mode of formation of $[NO^+][NO_3^-]$ ion-pairs, (c) the reaction of metals with gaseous dinitrogen tetroxide, (d) the stability of nitrites in the gaseous tetroxide, and (e) the reaction of metal oxides with liquid and gaseous dinitrogen tetroxide. The first four factors are discussed in this paper, and the fifth in the following paper.

(a) *Dipole Moments of N_2O_4 and NO_2 Molecules.*—The existence of ion-pairs $[NO^+][NO_3^-]$ in small concentration in liquid dinitrogen tetroxide was postulated in Part IV (*J.*, 1951, 1294) on the assumption that the N_2O_4 molecule in the liquid state has a zero dipole moment. However, since various authors give conflicting interpretations of their experimental data, it is necessary to assess the evidence in support of this zero value.

The first determination of the dipole moment of nitrogen dioxide was made by Ghosh and Mohanti (*Z. Physik*, 1929, **30**, 531) who found $\mu_{NO_2} = 0.62$ D for the gas. These calculations are of limited accuracy, since they were based on Nernst-bridge measurements of the dielectric constant ϵ by Badeker (*Z. physikal. Chem.*, 1901, **36**, 316). A later determination by Zahn (*Z. Physik*, 1933, **34**, 461) gave the values $\mu_{NO_2} = 0.39$ D and $\mu_{N_2O_4} = 0.55$ D; this work was criticised on grounds of interpretation by Williams, Schwingle, and Winnings (*J. Amer. Chem. Soc.*, 1934, **56**, 1427; 1936, **58**, 200) who deduced a zero value for $\mu_{N_2O_4}$, and a value of μ_{NO_2} which varied with temperature. Zahn (*Z. Physik*, 1935, **36**, 461) later agreed with this interpretation. However, independent measurements by

* Part XII, *J.*, 1952, 1399.

Schulz (*ibid.*, 1938, **109**, 517) led to the values $\mu_{\text{N}_2\text{O}_4} = 0.32 \text{ D}$ and $\mu_{\text{N}_2\text{O}_4} = 0.42 \text{ D}$; Schulz implied that the criticism of Zahn's interpretation by Williams *et al.* was incorrect. The assumption of a zero dipole for the N_2O_4 molecule therefore necessitates a temperature-variable dipole moment for the NO_2 molecule, whereas if μ_{NO_2} is assumed to be constant, a finite value for $\mu_{\text{N}_2\text{O}_4}$ results which is greater than that of μ_{NO_2} .

Zahn and Schulz assume that the contribution of N_2O_4 and NO_2 molecules to the total electrical polarisation is determined by the relative amounts present (f_1 and f_2 , respectively). Hence,

$$P = f_1(A_1 + B_1/T) + f_2(A_2 + B_2/T)$$

where A_1 and A_2 are the optical constants given by

$$A = \frac{M}{\rho} \left(\frac{n^2 - 1}{n^2 + 2} \right) = \frac{4}{3} \pi N \alpha_0$$

where N is Avogadro's number and α is the polarisability of the molecule. Assuming B_1 and B_2 to be constant ($B = 4\pi N \mu^2 / 9k$, where k is Boltzmann's constant), these authors determined values for $\mu_{\text{N}_2\text{O}_4}$ and μ_{NO_2} , but did not obtain sufficient data to enable a value for the dipole moment of each molecule to be calculated at any one temperature. If μ_{NO_2} varies with temperature, then Debye's equation cannot be applied. In order to compare the two sets of experimental data, the results of Williams *et al.* at two temperatures have been substituted in the above equation, and the values of $\mu_{\text{N}_2\text{O}_4}$ and μ_{NO_2} are given in Table 1.

TABLE 1.

	(a) $T_1 = 298^\circ \text{K}$, $T_2 = 318^\circ \text{K}$.					(b) $T_1 = 298^\circ \text{K}$, $T_2 = 343^\circ \text{K}$.				
$\mu_{\text{N}_2\text{O}_4}$	0.283	0.332	0.284	0.287	0.238	0.283	0.361	0.389	0.267	0.457
μ_{NO_2}	0.423	0.422	0.410	0.415	0.457	0.387	0.387	0.373	0.395	0.359
	(c) $T_1 = 318^\circ \text{K}$, $T_2 = 343^\circ \text{K}$.					(d) $T_1 = 298^\circ \text{K}$, $T_2 = 368^\circ \text{K}$.				
$\mu_{\text{N}_2\text{O}_4}$	0.469	0.348	0.360	0.321	0.391	0.333	0.391	0.306	0.393	0.471
μ_{NO_2}	0.352	0.389	0.370	0.387	0.382	0.341	0.341	0.342	0.337	0.339

The greater spread of results in the case of $\mu_{\text{N}_2\text{O}_4}$ no doubt arises from the smaller concentration of N_2O_4 molecules at the higher temperature, leading to greater errors in its evaluation. The means of the results in Table 1 are compared in Table 2 with Schulz's

TABLE 2.

	(a)	(b)	(c)	(d)
$\mu_{\text{N}_2\text{O}_4}$ { Schulz's results	0.416	0.416	0.415	0.411
{ Calc. from data of Williams <i>et al.</i>	0.28	0.38	0.39	0.39
μ_{NO_2} { Schulz's results	0.321	0.320	0.320	0.321
{ Calc. from data of Williams <i>et al.</i>	0.42	0.38	0.38	0.34

results (*loc. cit.*). If it is assumed that $\mu_{\text{N}_2\text{O}_4} = 0$, Schulz's data may be recalculated to give μ_{NO_2} at a series of temperatures (see Figure). Schulz applied an arbitrary correction of 5% for the contribution of atom polarisation, but this correction has been excluded from the results shown in the Figure. In view of the agreement shown, it is clear that the different conclusions of the above authors arise solely from differences in interpretation.

The values for the dielectric constant and refractive index of liquid dinitrogen tetroxide have been substituted into Onsager's equation (*J. Amer. Chem. Soc.*, 1936, **58**, 1486), *viz.*,

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

In comparison with the above values, this equation gives $\mu = 0.51 \text{ D}$ for dinitrogen tetroxide in the liquid state. In view of the limited applicability of this equation in media of low dielectric constant, the value obtained is reasonably close to that determined by Schulz. If the dipolar character of liquid dinitrogen tetroxide arises from a finite dipole in the tetroxide molecule, the agreement between the two independent $\mu_{\text{N}_2\text{O}_4}$ values would provide evidence that the N_2O_4 structure is the same in the gas as in the liquid state. However, this assumption is not justified (see below), and the above agreement is fortuitous.

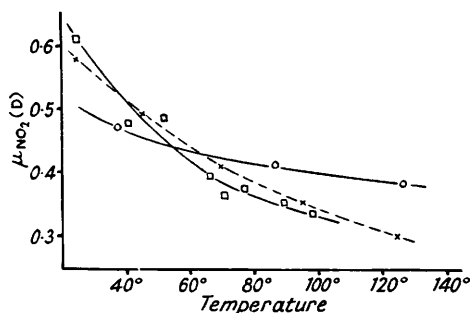
None of the results discussed above leads to a definite conclusion regarding the value for $\mu_{\text{N}_2\text{O}_4}$, but appropriate evidence is available from the measurements of ϵ made by Williams *et al.* (*loc. cit.*) on gaseous NO_2 - N_2O_4 mixtures, at a single temperature, in which the $\text{NO}_2/\text{N}_2\text{O}_4$ ratio was varied by change in pressure. Since no temperature change is involved, all dipole moments are constant, and the Debye equation may be applied directly to the experimental results. When this is done, a zero dipole moment for the N_2O_4 molecule is obtained.

This conclusion involves a temperature-variable dipole for the NO_2 molecule. Williams *et al.* (*loc. cit.*) have shown that this variation is larger than can be accounted for on the assumption that the molecule possesses two moments corresponding to two vibrational states. From ultra-violet absorption measurements, Harris and King (*J. Chem. Phys.*, 1940, **8**, 775) considered the possibility of nitrogen dioxide's possessing two low-lying electronic states of approximately the same energy. We have examined the variation in μ_{NO_2} from this point of view. When one activated state only is considered, we have

$$\mu^2 = \left[\frac{\mu_0^2 + K\mu_1^2 e^{-h\nu/kT}}{1 + Ke^{-h\nu/kT}} \right]$$

Since the observed moment μ decreases with increasing temperature, the moment μ_1 in the excited state must be less than the moment μ_0 in the ground state. On the

- Calc. from results of Schulz (*loc. cit.*).
 ○ Calc. from results of Zahn (*loc. cit.*).
 × Results of Williams *et al.* (*loc. cit.*).



assumption that the statistical weight factor K is unity, the difference between the values of μ/μ_0 at 300°K and 400°K has been calculated for a range of values of μ_1/μ_0 and $h\nu/kT$ (Table 3).

TABLE 3.

μ_1/μ_0	300°K		400°K		$(\mu/\mu_0)_{300} - (\mu/\mu_0)_{400}$
	$h\nu/kT$	μ/μ_0	$h\nu/kT$	μ/μ_0	
0.5	3.3	0.9911	2.5	0.9809	0.0102
	1.0	0.9304	0.75	0.9164	0.0140
	0.33	0.8892	0.25	0.8838	0.0054
0.1	3.3	0.9839	2.5	0.9651	0.0188
	1.0	0.8708	0.75	0.8433	0.0274
	0.33	0.7897	0.25	0.7784	0.0113
0.0	3.3	0.9820	2.5	0.9614	0.0206
	1.0	0.8851	0.75	0.8241	0.0310
	0.33	0.7624	0.25	0.7497	0.0230

The value of μ_0 is not known. However,

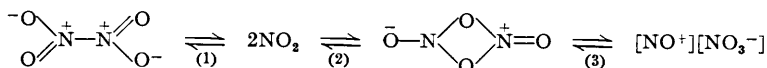
$$\mu_0 = (\mu_{300} - \mu_{400}) / [(\mu/\mu_0)_{300} - (\mu/\mu_0)_{400}]$$

and from the Figure, $\mu_{300} - \mu_{400}$ is approximately 0.3 D; the maximum value of the denominator (col. 6, Table 3) then gives a value of about 10 D for μ_0 . In order that the calculated value of μ_0 should be in a range of possible values, a degeneracy of the molecule in the activated state has been considered. Maximum variation in dipole moment with temperature occurs when $h\nu = kT$ (Van Vleck, *Phys. Reviews*, 1927, **29**, 729; **30**, 31) and also as μ_1/μ_0 approaches zero. The statistical weight K being assigned values of 1, 2, 3, and 4 (and on the assumption that $\mu_1/\mu_0 = 0$ and $h\nu = kT$ at 300°K), the differences

between the two values of μ/μ_0 are 0.031, 0.042, 0.046, and 0.048, respectively. Variation of K within reasonable limits does not therefore bring about the necessary decrease in μ_0 , and it is not possible to explain the temperature variation in μ_{NO_2} by assuming one excited state; the assumption of three electronic levels involves too many unknown parameters to permit corresponding calculations to be made. However, the considerable amount of evidence for the symmetrical structure of the N_2O_4 molecule in the solid and in the gaseous state supports the assumption of a zero value for $\mu_{\text{N}_2\text{O}_4}$ (and thus a temperature-variable μ_{NO_2}) in the liquid state also.

(b) *Mode of Formation of $[\text{NO}^+][\text{NO}_3^-]$ Ion-pairs.*—Of the various possible ion-pairs, the $[\text{NO}^+][\text{NO}_3^-]$ pair has been postulated, since almost all the chemical reactions of the N_2O_4 molecule are in accord with this formulation. In the absence of any plausible mechanism involving either intermolecular or intramolecular rearrangements of the N_2O_4 molecules themselves, atom transfer may be considered to occur subsequent to the initial homolytic (i) or heterolytic (ii) dissociation of N_2O_4 molecules: (i) $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2 + \text{NO}_2$, (ii) $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2^+ + \text{NO}_2^-$, and the mode which predominates is determined by the dielectric constant of the medium (Waters, *J.*, 1942, 153).

(i) *Homolytic dissociation.* If atom transfer follows this mode, it must result from impact between NO_2 molecules, a type of reaction which occurs also in the equilibrium $2\text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{BrF}_4^-$ (Banks, Emeléus, and Woolf, *J.*, 1949, 2861). A molecule having the structure proposed by Longuet-Higgins (*Nature*, 1944, 153, 408) could serve as an intermediate, thus

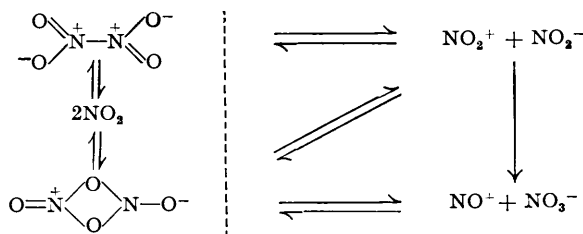


Since no dipolar constituent is present in the gaseous state (see below), an intermediate compound of this structure is more likely than the unsymmetrical molecule $\text{ON}\cdot\text{O}\cdot\text{NO}_2$ considered by Seel (*Z. anorg. Chem.*, 1952, 269, 103). The existence of an intermediate compound having a different structure from the parent molecules has a direct analogy in dinitrogen trioxide (Addison, Lewis, and Thompson, *J.*, 1951, 2838). This interpretation however is incomplete, since it does not provide any reason why these particular ions should be formed.

(ii) *Heterolytic dissociation.* The extent of ionic dissociation of N_2O_4 broadly follows the ϵ ranges suggested by Waters (*loc. cit.*). Thus, in pure dinitrogen tetroxide ($\epsilon = 2.42$), ionic dissociation occurs to the extent of only about 0.1%; the rate of reaction with metals is decreased by the dilution factor only on dilution of the tetroxide with liquids (*e.g.*, benzene) of similar low dielectric constant. In glacial acetic acid ($\epsilon = 7.1$) containing sodium acetate, ionic dissociation is increased sufficiently to enable the presence of ions to be detected by electrolysis (Angus, Jones, and Philips, *Nature*, 1949, 164, 433). The addition of diethylnitrosamine ($\epsilon = 42.5$) increases the electrical conductivity of liquid dinitrogen tetroxide by a factor of 10^8 (Part VI, *J.*, 1951, 1303). In solution in pure nitric acid, dinitrogen tetroxide is completely dissociated into ions (Goulden and Miller, *J.*, 1950, 2620), and in sulphuric acid ($\epsilon = 110$; Brand, James, and Rutherford, *J. Chem. Phys.*, 1952, 20, 530) ionisation is again complete (Gillespie, Graham, Hughes, Ingold, and Peeling, *J.*, 1950, 2504).

Such dissociation reactions involve a simple change from equal to unequal sharing of the bonding electrons, so the first stage in the heterolytic dissociation of dinitrogen tetroxide gives rise to NO_2^+ and NO_2^- ions. Detailed studies in each of the above liquid systems have identified the ions present as NO^+ and NO_3^- ; the reaction $\text{NO}_2^+ + \text{NO}_2^- \longrightarrow \text{NO}^+ + \text{NO}_3^-$ must therefore follow immediately the primary heterolytic dissociation, and be irreversible. The high oxidising power of the nitronium ion, and its close proximity to the nitrite ion in the $[\text{NO}_2^+][\text{NO}_2^-]$ ion-pair would render the two groups incompatible. Oxygen-atom transfer is then an oxidative process which is consistent with the chemical properties of the ions concerned. Since it is the initial heterolytic dissociation, and not the oxidative process, which is influenced by ϵ of the medium, the ultimate ionic products of dissociation are independent of medium.

The equilibria existing in dinitrogen tetroxide may then be represented by the following scheme :



All the equilibria shown occur in the liquid state; only those to the left of the vertical broken line occur in the gaseous state. The complete absence of nitrite ion as a reaction product indicates that the oxidation of NO_2^- by NO_2^+ takes place before either ion is able to react independently with other reactants introduced into the system. Reactions with ethylenic linkages can be explained on the basis of the polar nature of the nitrogen in the tetroxide (Levy and Scaife, *J.*, 1946, 1093) without assuming the existence of discrete NO_2^+ and NO_2^- ions (Ingold, *Nature*, *loc. cit.*); it is significant that dinitro-compounds are formed in gaseous reactions also, when no ion-pairs exist. The possibility that nitronium and nitrite ions are produced on impact is not supported elsewhere in the chemistry of dinitrogen tetroxide.

(c) *Reaction of Metals with Gaseous Dinitrogen Tetroxide.*—In their study of gaseous N_2O_4 - NO_2 mixtures, Williams *et al.* (*loc. cit.*) determined the value of μ_{NO_2} for a range of pressures and at a single temperature. The values of μ_{NO_2} and $\mu_{\text{N}_2\text{O}_4}$ were constant and independent of pressure, indicating that only these two components are present in the gaseous phase. The concentration of a third ionic component would vary with pressure, and its presence would lead to variations in μ_{NO_2} and $\mu_{\text{N}_2\text{O}_4}$. The same conclusion follows independently from a consideration of the low dielectric constant in the gaseous state.

If a second mechanism, involving N_2O_4 and NO_2 molecules only, operates in the liquid state, then reaction with gaseous mixtures (which contain no ion-pairs) should follow the same mechanism to give the same reaction products as with the liquid. When sodium is burnt in the gas (Holt and Sims, *J.*, 1894, 65, 432; Dulong, *Ann. Chim. Phys.*, 1816, 2, 317) a mixture of sodium nitrite and sodium nitrate is produced. At the temperature of burning sodium the gaseous phase contains oxygen and nitric oxide, and reaction with the latter gives rise to nitrite (following paper). At 300°, metallic zinc is converted into zinc oxide by nitrogen dioxide (Sabatier and Senderens, *Compt. rend.*, 1892, 115, 236). The reaction of metallic sodium and zinc with gaseous N_2O_4 - NO_2 mixtures has therefore been studied at temperatures below 140° (at which temperature dissociation of NO_2 becomes appreciable).

(i) The gas mixture was passed, at 60–80° and at atmospheric pressure, over metallic sodium. During about 15 min. the metal acquired a thin coating of white solid; after this, the coating was sufficiently cohesive to prevent further reaction. The coating was scraped from the metal, and its X-ray powder photograph was found to be identical with that of pure sodium nitrate.

(ii) The gas mixture was passed, at 120–140°, over a block of pure zinc. The metal developed a crust of white solid, which did not inhibit the reaction. Spectrophotometric analysis of the product showed the absence of nitrite, and chemical analysis confirmed that the product was pure zinc nitrate. A similar reaction, carried out at 60–80°, gave a yellow viscous liquid identical with a mixture of zinc nitrate and the compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{O}_4$ (Part VII, *J.*, 1951, 2829). When this product was heated at 100°, dinitrogen tetroxide was evolved and pure zinc nitrate remained. At the temperature (300°) used by Sabatier and Senderens (*loc. cit.*) anhydrous zinc nitrate decomposes rapidly to zinc oxide (Part VII, *loc. cit.*).

Since the products of reaction in the gaseous and in the liquid state are identical, it is permissible to consider a mechanism of reaction in the liquid state which does not involve ion-pairs.

(d) *Stability of Nitrites in Gaseous Dinitrogen Tetroxide.*—The close analogy drawn above between reactions in the liquid state, and in the gaseous state below 140° , is only justified if nitrites are also stable in contact with gaseous N_2O_4 - NO_2 mixtures over a corresponding temperature range. Oswald (*Ann. Chim.*, 1914, 1, 44) found that oxidation occurred at 100° , and also took place very slowly at room temperature. This reaction has been re-examined; the experimental conditions and results are given below :

Expt. No.	1	2	3	4	5	6	7
Temp.	40°	70°	85°	100°	100°	122°	200°
Reaction period (hours)	6	6	40	7	7	43	3
% conversion into nitrate	0.0	0.0	0.85	0.5	0.0	5.4	49.5

The nitrate content of the product was determined by ultra-violet spectrographic analysis (*J.*, 1952, 338). At the lower temperatures the oxidation of nitrite is negligible over long periods, although on prolonged contact (Expt. 3) slight oxidation does occur. At temperatures above the dissociation temperature of nitrogen dioxide (Expt. 7) oxidation is considerable; reactions of this type are considered in detail in the following paper. The dissociation temperature of the NO_2 molecule is normally quoted as 140° , but Expt. 6 implies that slight dissociation occurs below this temperature.

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