Dinitrogen Trioxide. Part XII.[1] The Liquid Dinitrogen Trioxide Solvent System

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The relative permittivity and electrolytic conductivity of N_2O_3, N_2O_4, and their mixtures have been measured. Values for the refractive index and dipole moment of N_2O_3 have been obtained. The extent of the self-ionization $N_2O_3 \rightleftharpoons NO^+ + NO_2^-$ has been estimated and its influence on chemical reactions in this solvent is discussed. The influence of N_2O_4 and organic solvents on the reactions of N_2O_3 are considered.

ALTHOUGH N_2O_3 has been known since 1816 many of its physical properties are still unknown. When considering N_2O_3 as a solvent system, two properties are extremely important, *i.e.* the relative permittivity and the electrolytic conductivity. The former determines the degree of ionization of a solute while the latter reflects the extent of any self-ionization which is normally necessary for solvolytic reactions to occur. We now report a detailed study of these and other properties which are relevant when considering N_2O_3 as a solvent system.

Relative Permittivity Measurements.—The relative permittivities of N_2O_3 (ε_3), N_2O_4 (ε_4), and their mixtures were measured over a range of temperatures limited by the freezing point of the system on the one hand [2] and its vapour pressure on the other.[3] The results for N_2O_4 are presented in Table 1. The values of ε_4 are typical for

TABLE 1

Some physical properties of N_2O_4

t/°C	+20	+10	0	−10	−20
ε_4	2·44	2·45	2·47	2·48	2·49
P_4/cm^3 mol^{-1}	20·6	20·4	20·3	20·1	19·9
10^{12} κ_4/Ω^{-1} cm^{-1}	5·03	3·32	2·18	1·38	0·84

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[1] Part XI, A. W. Shaw and A. J. Vosper, *J.C.S. Dalton*, 1972, 961.

[2] I. R. Beattie, S. W. Bell, and A. J. Vosper, *J. Chem. Soc.*, 1960, 4796.

[3] I. R. Beattie and A. J. Vosper, *J. Chem. Soc.*, 1960, 4799.

a nonpolar liquid and we observed little variation with temperature. By contrast Audinos[4] has recently reported values for ε_4 varying from 2·003 at 5 °C to 2·787 at 25 °C. A puzzling feature of these measurements is that the molar polarization (P_4) calculated from their results was not inversely proportional to the absolute temperature as is normally the case. Since N_2O_4 has a symmetrical structure in the gas[5] and solid[6] it is unlikely to possess a permanent dipole in the liquid. Although NO_2 is a polar molecule its concentration is far too low[7] to account for such a large temperature variation. The same applies to other possible species such as NO^+ and NO_3^- in the form of ion-pairs or solvated ions. The reason for the disagreement between the two sets of results is not clear but all previous work has given values of ε_4 close to 2·4 with little temperature variation in agreement with our data.[8,9]

The results for N_2O_3 are given in Table 2. The values of ε_3 are typical of a polar but unassociated liquid and exceed slightly the corresponding values for NH_3 or NOCl at the same temperature. On this evidence alone, N_2O_3 might be expected to act as an ionizing solvent. The molar polarization (P_3) increased slightly with increasing temperature as is the case for other polar liquids, *e.g.* SO_2 and NH_3.

TABLE 2

Some physical properties of N_2O_3

t/°C	−30	−40	−50	−60	−70
ε_3	25·41	26·65	28·01	29·50	31·13
P_3/cm^3 mol^{-1}	46·5	46·3	46·0	45·7	45·3
$10^8\ \kappa_3/\Omega^{-1}$ cm^{-1}	13·1	10·2	7·85	5·86	4·25
$10^{12}\ K'$/mol^2 dm^{-6}	4·70	4·17	3·76	3·30	2·87
$10^{13}\ K$/mol dm^{-3}	2·46	2·16	1·92	1·67	1·43

For N_2O_3–N_2O_4 mixtures the relative permittivity increased with the mole fraction of N_2O_3 in a non-linear manner but the molar polarization increased rapidly at first then reached an almost constant value (see Figure 1). Clearly the molar polarization of the polar N_2O_3 decreases with increasing concentration and the molar polarization of the mixture cannot be calculated assuming additivity of the pure components.

Refractive Index Measurements.—The refractive index of N_2O_3 could not be directly measured owing to its instability. The refractive index of N_2O_3–N_2O_4 mixtures containing up to 47 mol % of the former were obtained at room temperature, using the method of minimum deviation. The results for N_2O_4 were in good agreement with the literature values.[8] It was found experimentally that the molar refraction of an N_2O_3–N_2O_4 mixture could be expressed as the weighted sum of the molar refraction of the two components *i.e.*

$$R = \frac{n^2 - 1}{n^2 + 2}\frac{(M_3x_3 + M_4x_4)}{\rho} = R_3x_3 + R_4x_4$$

R, n, M, x, and ρ represent the molar refraction, refractive index, molecular weight, mole fraction, and density respectively. The subscripts 3 and 4 refer to the pure components N_2O_3 and N_2O_4 respectively while quantities without a subscript correspond to the mixture. A plot of R against x_3 gave a straight line which could be extrapolated to $x_3 = 1$ in order to estimate values of R and n for pure N_2O_3. Since N_2O_3 absorbs in the red region of the spectrum, the most reliable values were obtained using the mercury blue and blue-green lines. The final values for the refractive index of N_2O_3 were $n^{18}_{453\cdot8} = 1\cdot410$ and $n^{18}_{491\cdot6} = 1\cdot402$. The refractive index at infinite wavelength was obtained using the Cauchy equation ($n^{18}_{\infty} = 1\cdot373$). Because of the experimental difficulties and the extrapolation of the results, a high precision cannot be claimed.

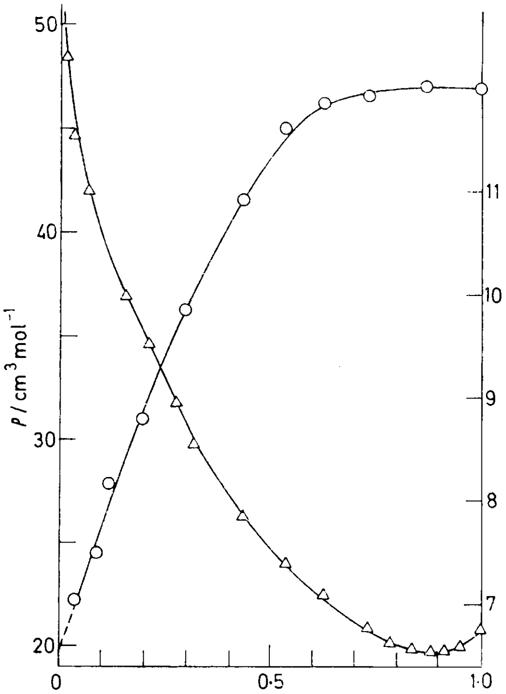

FIGURE 1 Molar polarization and electrolytic conduction of the N_2O_3–N_2O_4 system at −20 °C; ○ = molar polarization, △ = electrolytic conduction

These results suggest that the nonlinear variation of the molar polarization with composition (Figure 1) is due to the orientation polarization rather than the distortion component.

For N_2O_4, the molar polarization (P_4) and molar refraction were 20·2 cm^3 mol^{-1} and 15·4 cm^3 mol^{-1} respectively. These are in good agreement with previous results[8] since P_4 is 20·5 cm^3 mol^{-1} and not 26·5 cm^3 mol^{-1} as stated in the paper. The difference between P_4 and R_4 suggests a significant atomic polarization contribution and possibly the presence of ion-pairs as previously suggested.[8]

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[4] R. Audinos, *J. Chim. phys.*, 1972, **69**, 1263.

[5] B. W. McClelland, W. G. Bruce, and K. Hedberg, *J. Chem. Phys.*, 1972, **56**, 4541.

[6] J. S. Broadley and J. M. Robertson, *Nature*, 1949, **164**, 915.

[7] A. J. Vosper, *J. Chem. Soc.* (*A*), 1970, 2191.

[8] C. C. Addison, H. C. Bolton, and J. Lewis, *J. Chem. Soc.*, 1951, 1294.

[9] H. Schlundt, *J. Phys. Chem.*, 1904, **8**, 122.

For N_2O_3, the corresponding values of P_3 and R_3 were estimated to be 48 and 13 cm^3 mol^{-1} at room temperature. To obtain these values, it was necessary to extrapolate the results for the density[10] and relative permittivity of N_2O_3 from about -30 °C to room temperature. The large difference between P_3 and R_3 confirms that this molecule has a significant dipole moment.

The Dipole Moment of N_2O_3.—The dipole moment of N_2O_3 was estimated from the values of P_3 and R_3 using the Onsager relationship and a value of $2{\cdot}7 \pm 0{\cdot}3$ D was obtained (1 D = $3{\cdot}336 \times 10^{-30}$ C m). This exceeds the value for gaseous N_2O_3[11] (*i.e.* $2{\cdot}12 \pm 0{\cdot}01$ D) but in view of the uncertainty in the values of P_3 and R_3 and the approximations involved in the Onsager equation, the agreement is as good as can be expected.

A more reliable method of obtaining the dipole moment was to measure the relative permittivity of dilute solutions of N_2O_3 in the nonpolar solvent CCl_4. Measurements were made between the freezing point of the solution and room temperatre. Dissociation of the N_2O_3 was prevented by maintaining an elevated pressure of NO above the liquid. Measurements were made at several different concentrations of N_2O_3 (up to a maximum of 5 mol %) and the values for P_3 were extrapolated to infinite dilution. A plot of these values against the reciprocal of the absolute temperature gave the expected linear relationship and the dipole moment was calculated from the slope, using the method of least squares. In this way the difficulties concerning the exact value for the refractive index of N_2O_3 were avoided. The final result for the dipole moment of N_2O_3 was $2{\cdot}07 \pm 0{\cdot}03$ D in good agreement with the gas phase results.[11] Theoretical calculations have shown the molecule is polar in the sense $NO^{\delta+}$–$NO_2^{\delta-}$.[12]

Electrolytic Conductivity Measurements.—The electrolytic conductivity of liquid N_2O_4 (κ_4) valued between 5×10^{-13} and 10^{-12} Ω^{-1} cm^{-1} at room temperature. The exact value is probably influenced by traces of impurities and the lower value is probably the more accurate. For a given sample of N_2O_4 it was found that $\log_{10}\kappa_4$ was inversely proportional to the absolute temperature in agreement with previous work[13-15] but the temperature variation was much less than that reported recently by Audinos.[4] Some typical results are given in Table 1. The low value of κ_4 shows that solvated ions can only be present in small concentrations but since ε_4 has a low value the concentration of ion-pairs could be much higher.

The addition of small amounts of N_2O_3 causes a rapid increase in the electrolytic conductivity[16] (see Figure 1). In our opinion, this could provide a useful method for detecting NO and other impurities in N_2O_4 for use as an oxidant in rocket propellant systems. At a given temperature the electrolytic conductivity increases with the concentration of N_2O_3 reaching a maximum at about 90 mol % and then decreases until it reaches the value for pure N_2O_3 (see Figure 1). The maximum conductivity does not necessarily correspond to the greatest concentration of ions since it also depends on the viscosity of the medium and the ionic mobilities of the ions. It can be shown that the former has little effect (see later discussion). If one assumes that the ionic mobilities of NO_2^- and NO_3^- are equal in this solvent it follows that the concentration of ions corresponding to the maximum conductivity is approximately twice that occurring in pure N_2O_3. The NOCl–N_2O_4 system behaves in a similar way with a maximum conductivity again near 90 mol % NOCl.[17]

The addition of N_2O_3 increases the relative permittivity of the system and this may result in the conversion of ion-pairs to solvated ions. This is equivalent to a displacement of the equilibrium $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$ towards the right-hand side. At high N_2O_3 concentrations this is inhibited by the decreasing concentration of N_2O_4.

In order to measure the conductivity of N_2O_3 it is essential that N_2O_4 is absent. At each temperature measurements were made with increasing partial pressures of NO above the liquid until a constant value was obtained which was characteristic of N_2O_3 (see Table 2). The results show that N_2O_3 has a significant electrolytic conductivity suggesting some self-ionization. The most likely process involves the simple heterolytic dissociation of the N–N bond, *i.e.* $N_2O_3 \rightleftharpoons NO^+ + NO_2^-$. This in in agreement with the polarity of N_2O_3[12] and its chemical reactions.[18] There is no evidence for the presence of other ions, *e.g.* $2N_2O_3 \rightleftharpoons 2NO_2^+ + N_2O_2^{2-}$.

In order to calculate the extent of this self-ionization the ionic mobilities of the NO^+ and NO_2^- ions are required. These are not available so it was necessary to make the crude assumption that they are equal to the mobility of the NO_3^- ion in this solvent. In fact the ionic mobilities of different ions do not vary greatly unless special conduction mechanisms are present. It is now possible to calculate the concentration of the ions assuming the validity of Walden's rule. The method of calculation was very similar to that previously used to estimate the concentration of ions in N_2O_4.[15] This calculation requires the viscosity of N_2O_3 over the appropriate temperature range. The viscosity of N_2O_3–N_2O_4 mixtures containing up to 87 mol % of the former has been reported.[19] At constant temperature, the viscosity varied little with composition and the results were extrapolated to obtain values for pure N_2O_3. In this way approximate values for the ionic product K' given by $K' = [NO^+][NO_2^-]$ were obtained and the smoothed values are given in Table 2. The equilibrium constant

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[10] A. W. Shaw and A. J. Vosper, *J. Chem. Soc.* (*A*), 1971, 2708.

[11] A. H. Brittain, A. P. Cox, and R. L. Kuczkowski, *Trans. Faraday Soc.*, 1969, **65**, 1963.

[12] J. R. Yardle and N. S. Hush, unpublished work quoted in ref. 11.

[13] C. C. Addison and J. Lewis, *J. Chem. Soc.*, 1952, 4079.

[14] C. C. Addison, J. Allen, H. C. Bolton, and J. Lewis, *J. Chem. Soc.*, 1951, 1289.

[15] R. S. Bradley, *Trans. Faraday Soc.*, 1956, **52**, 1255.

[16] C. C. Addison, J. Lewis, and R. Thompson, *J. Chem. Soc.*, 1951, 2838.

[17] C. C. Addison and J. Lewis, *J. Chem. Soc.*, 1951, 2843.

[18] A. J. Vosper and his co-workers, unpublished work.

[19] D. B. Brice and N. Fishman, *Amer. Rocket Soc. J.*, 1959, 354.

(K) for $N_2O_3 \rightleftharpoons NO^+ + NO_2^-$ was also calculated. Both K' and K varied only slightly with temperature since the observed variation of the electrolytic conductivity with temperature was mainly due to the changing viscosity of the medium. A plot of $\log_{10} K$ against $1/T$ gave the expected linear relationship from which it was estimated that $\Delta H^\circ \sim 7$ kJ mol^{-1} and $\Delta S^\circ \sim -200$ J mol^{-1} K^{-1}. The negative value for ΔS° is to be expected since the ions produced will cause an ordering of the local polar solvent molecules. Its magnitude is similar to that for the self-ionization of other polar solvents, *e.g.* NH_3.[20] The value for ΔH° is surprisingly small being considerably less than the enthalpy change for the homolytic dissociation of liquid N_2O_3.[21] This smaller value presumably reflects a greater interaction of the solvent with the ions than with the radicals.

The enthalpy and entropy of solvation of the two ions were estimated using the thermodynamic cycle illustrated in Figure 2. The results for the heat of evaporation of N_2O_3 have been published [22] and those for the dissociation of gaseous N_2O_3 are based on recent work.[18] The ionization potential of NO is accurately known [23] and recent determinations of the electron affinity of NO_2 [24,25] suggest a value near 236 kJ mol^{-1}. The corresponding entropy changes were calculated from the JANAF thermodynamic tables. The values estimated for the enthalpy and entropy of solvation of the two ions were *ca.* −720 kJ mol^{-1} and −440 J K^{-1} mol^{-1} respectively. The major uncertainty concerns the enthalpy and entropy changes for the self-ionization of N_2O_3 estimated in this paper.

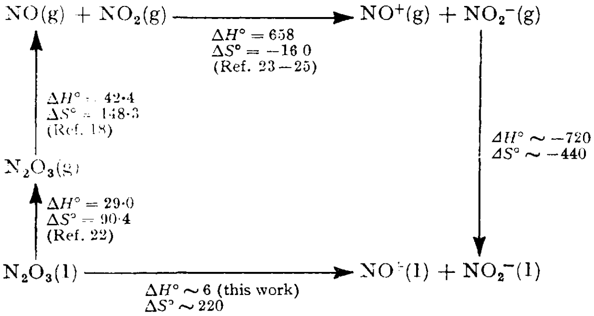

FIGURE 2 Thermodynamic cycle for obtaining the enthalpy and entropy of solvation of NO^+ and NO_2^- in N_2O_3. Standard states are the pure liquids and gases at a pressure of 101·325 kN m^{-2} (one atmosphere). The units for ΔH° and ΔS° are kJ mol^{-1} and J mol^{-1} K^{-1} respectively

The heat of solvation is smaller in magnitude (*i.e.* neglecting the negative sign) than the estimated heat of hydration. Thus the ion–solvent interaction energies appear to be less than for water. The entropy of solvation is larger in value than the estimated entropy of hydration. This is not surprising since water has a relatively ordered structure due to hydrogen bonding and this is disrupted in the vicinity of ions. Thus the introduction of the gaseous ions into the solvent produces a greater degree of order for N_2O_3. If these conclusions apply to other ions they may explain the low solubility of ionic compounds in N_2O_3 reported in the next section.

Dinitrogen Trioxide as a Solvent.—N_2O_3 Has a useful temperature range from the freezing point [2] (−100·6 °C) to about −30 °C when dissociation becomes significant, at atmospheric pressure. It is possible to use N_2O_3 up to room temperature provided an elevated pressure of NO is maintained above the liquid.

In spite of the relatively high dielectric constant we have found that most ionic compounds have little solubility in this medium (less than 0·1%). This included the alkali-metal halides, nitrates, chlorates, perchlorates, and sulphates as well as the alkali-metal nitrites and simple nitrosonium salts (*e.g.* perchlorate and bisulphate) which might be anticipated to function as bases and acids respectively, in this solvent. Tetra-alkylammonium salts were somewhat soluble and behaved as weak electrolytes but it was found that solvolytic reactions commonly occurred. The insolubility of simple ionic compounds suggests that in spite of its dipole moment, the ion–solvent interaction energies are generally less than the lattice energy of the solutes. Solid transition-metal compounds were also highly insoluble. This probably reflects the inability of N_2O_3 to donate an electron pair to the metal ion. The available evidence suggests that N_2O_3 is acidic rather than basic, in the Lewis sense.[18]

N_2O_3 has little tendency to form solvates and such compounds would be expected to be unstable owing to the instability of the solvent molecules. Some compounds which appear to be solvates can be obtained at low temperatures, *e.g.* $M(NO_2)_2,2N_2O_3$ (M = Zn or Hg) but these are best formulated as nitrosonium salts, *i.e.* $(NO)_2[M(NO_2)_4]$.[18]

The Influence of N_2O_4 *and Organic Solvents.*—The chemical reactions of N_2O_3 can be considerably influenced by the presence of N_2O_4. Studies of the chemical reactions of N_2O_3–N_2O_4 mixtures suggest that reactions which involve ions give products characteristic of N_2O_4 rather than N_2O_3, unless the concentration of the former is very small. The addition of N_2O_4 increases the concentration of NO_2 radicals and therefore increases the velocity of reactions proceeding by a radical mechanism. Since N_2O_4 is a stronger oxidizing agent than N_2O_3 its presence can result in the oxidation of the initial reaction products. This appears to occur in the reactions of N_2O_3 with phenols. Similarly the initial products of reactions involving N_2O_3 are often metal nitrites but these are readily oxidized to the nitrate by N_2O_4.*

Most organic solvents are miscible in all proportions with N_2O_3. Exceptions are provided by alkane and

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* Although highly ionic nitrites, *e.g.* the alkali-metal salts, are unaffected by N_2O_4 others, *e.g.* the Ag^I, Tl^I, and Ni^{II} salts, are oxidized by N_2O_4 to the nitrate.

[20] H. D. Muller and F. C. Schmidt, *J. Amer. Chem. Soc.*, 1951, **73**, 5575.

[21] A. W. Shaw and A. J. Vosper, *J. Chem. Soc.* (*A*), 1971, 1592.

[22] A. J. Vosper, *J. Chem. Soc.* (*A*), 1971, 1589.

[23] C. Jungen and E. Miescher, *Canad. J. Phys.*, 1969, **47**, 1769.

[24] D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, *Chem. Phys. Letters*, 1972, **15**, 257.

[25] C. B. Leffert, W. M. Jackson, and E. W. Rothe, *J. Chem. Phys.*, 1973, **58**, 5801.

alkene solvents and by carbon disulphide. Many reactions which are insignificant with neat N_2O_3 will proceed with N_2O_3 dissolved in a suitable solvent. Studies of the electrolytic conductivity of N_2O_3 in organic solvents has shown that for nitroethane and acetonitrile there is only a slight increase in the concentration of ions while for methylene chloride and toluene the concentration of ions is decreased. Thus N_2O_3 differs sharply from N_2O_4 where the addition of solvents with a high relative permittivity or strong donor properties increase the conductivity of the solution considerably.

The addition of solvents with donor properties does have the important result that the reactant and/or the products may then be soluble in the medium. This is particularly true of transition metals and their compounds. Many reactions in neat N_2O_3 produce only a surface film of product which inhibits further reaction. For reactions which are violent with neat N_2O_3, the addition of an inert organic solvent may prevent local heating and the decomposition of the N_2O_3.

The Reactions of N_2O_3.—Virtually all the reactions which occur in pure N_2O_3 or in N_2O_3 solutions involve this oxide or species which are derived from it. The polar N_2O_3 molecule is itself reactive and can undergo heterolytic and homolytic dissociation producing NO^+ and NO_2^- ions and NO and NO_2 radicals respectively.

It is well known that N_2O_3 will function as an electrophilic nitrosating agent, *e.g.* with alcohols, amines, phenols, and other organic compounds. It is difficult to decide whether such reactions involve N_2O_3 or the NO^+ ion. It appears that with the stronger nucleophiles, direct attack by N_2O_3 predominates because of its much higher concentration but with less reactive systems reaction is initiated by NO^+ since this is a stronger electrophile.

In other cases there is evidence that the reaction involves ions. The reaction of N_2O_3 with certain metals produces metal nitrites and NO. The latter is probably produced by the reduction of NO^+ at the metal surface.

Some reactions undoubtably proceed by a free-radical mechanism. The reaction of N_2O_3 with certain *p*-block halides shows an induction period followed by a vigorous and uncontrollable reaction. This suggests a free-radical chain reaction. The orientation of the addition of N_2O_3 to unsymmetrical alkenes gives clear evidence that the attack is initiated by the NO_2 radical.

Although N_2O_3 is less reactive than the higher nitrogen oxides it is capable of reacting with a variety of inorganic and organic compounds. These reactions will be reported later.

EXPERIMENTAL

The purification of NO, NO_2, and the solvents and all physical measurements were conducted in an all-glass high-vacuum system fitted with greaseless stopcocks and joints. NO_2 Was dried by several distillations from phosphoric oxide and its weight determined after distillation from a weighed ampoule. The weight of NO was determined indirectly using a gas burette and was dried by passing through phosphoric oxide prior to use.

Capacitance measurements were made using a Wayne–Kerr B221 universal bridge. The cell consisted of two co-axial nickel cylinders separated by a small gap with PTFE spacers. Its capacitance was determined over a range of temperatures using water, methanol, and liquid ammonia as standards.

Conductivity measurements were made using the Wayne–Kerr bridge or a Victoreen Picometer model 474 for the lower ranges. Previous work has shown that any back e.m.f. in the d.c. measurements is small. The a.c. and d.c. measurements were in good agreement in their common range. The cell was of conventional design with sheet platinum electrodes. The cell constant was determined using aqueous KCl solution and measurements with ethanol confirmed that there was negligible temperature variation.

Refractive index measurements used a hollow glass prism and a simple visible spectrometer. The method of minimum deviation was employed similar to that described for N_2O_4.

Solubility measurements were made by shaking the solid with N_2O_3 at -30 °C for several hours. The liquid was forced through a No. 4 sinter and the nitrogen oxides were removed *in vacuo*. The weight of any residual solid was then determined.

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