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Nitrous Acid Chemistry

Anhydrous Dinitrogen Trioxide Solutions for Brønsted Acid Free Nitrous Acid Chemistry

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Abstract: Dinitrogen trioxide, N_2O_3, is readily prepared and stabilized in high concentrations in dry organic solvents at normal working temperatures. These conditions allow for facile acid and water free nitrosation and nitration reactions for which three examples are given here: the preparation of benzenediazonium nitrite, $[PhN_2][NO_2]$; nitrosyl chloride, NOCl, and nitrosylsulfuric acid, $(ONOSO_3H)$.

Introduction

Nitrosation and nitration are abiding challenges for green chemistry. The strongly acidic and oxidizing environment of conventional nitrous acid mediated reactions is problematic for many substrates and can engender a host of by-products. At the heart of this chemistry is dinitrogen trioxide (N_2O_3), an oxide of nitrogen that reversibly condenses as an azure blue liquid when the radicals nitric oxide (NO) and nitrogen dioxide (NO_2) are free to combine at temperatures below –40 °C.[1] Nitric oxide and dinitrogen trioxide are also termed nitrogen monoxide and nitrogen trioxide; here the former will be used without radical dots. It dissociates readily upon warming and as such has been little studied, at least compared to its constituent gas species or dinitrogen tetroxide. Most of what is known of its chemistry is in connection with nitrous acid, which is its hydrated form [Equation (1)].

$$2\,\mathrm{HONO} \rightleftharpoons N_2O_3 + H_2O \tag{1}$$

The K_{eq} of this reaction in water is estimated[2] to be 3×10^{-3} M^{-1}, which is sufficient to lend a pale blue coloration to concentrated nitrous acid.

Nevertheless, it has been known for over a century that dinitrogen trioxide can be stabilized by dissolving it in an organic matrix, provided that the solvent is either polar or aromatic with no active hydrogens. The earliest report of such an effect, to the best of our knowledge, is from Cundall[3] in 1895, who dissolved it in various chlorinated solvents. Joan Mason spectroscopically characterized dissolved N_2O_3 at low temperatures,[4] but the most recent and thorough study of the solutions themselves has been the work of A. J. Vosper, who published a series of papers from 1960 to 1974, which describe how solutions of N_2O_3 can remain stable even at room temperature. Vosper reports a few chemical experiments in which these solutions are treated with primary and secondary amines, and some metals. Yet the stabilizing effect of organic solutions on N_2O_3 remains largely underutilized, and although re-discovered or noted obliquely from time to time,[5–7] it has not been further developed.

In our laboratory, we have found that organic solvent stabilized N_2O_3 can be easily prepared at molar concentrations with reliable purity, often superior to prior reports and without the use of cryogens. Furthermore, it may be stored and used at room temperature, or higher, to perform a wide variety of different chemical operations, from nitration/nitrosation to oxidation and adduct formation. In this paper we describe our methods for the preparation and handling of these solutions, as well as three original examples of convenient uses for the solutions in the preparation of otherwise tricky derivatives: benzenediazonium nitrite, pure nitrosylsulfuric acid, and nitrosyl chloride.

Results and Discussion

N_2O_3 in Organic Solvents

Shaw and Vosper report[8] that nearly pure N_2O_3 can be prepared by condensing NO_2 gas as solid N_2O_4 at –78 °C in the upper regions of a long vessel submerged in a dry ice/ethanol bath, then passing NO gas over this such that liquid N_2O_3 may condense as it forms, pooling in the bottom of the vessel. The solvent is added afterwards. Although this is effective it is a cumbersome operation that limits the throughput of the preparation and requires extensive use of cryogens.

We have found that a simple and reliable alternative is to use a system of dynamic absorption, in which an ice-chilled solvent is treated with small alternating doses of oxygen and NO while under gentle stirring (see Experimental for details). NO gas reacts with oxygen to produce NO_2, which combines with the next round of NO at the surface of the solution to form N_2O_3. The N_2O_3 dissolves rapidly, allowing more gas to be introduced. In this way the chemist can add over a liter of gas

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to only a few milliliters of solvent without the application of high pressure. For proper use, it is crucial to understand that solutions of N_2O_3 are in a state of equilibrium with their atmosphere [Equation (2)].

$$2\,N_2O_{3(sol)} \rightleftharpoons N_2O_{4(sol)} + 2NO_{(g)} \tag{2}$$

In the gas phase, the equilibrium constant favors dissociation to NO and NO_2, at 25 °C, $K_{eq} = 1.916$,[9] while the presence of solvent shifts the equilibrium to the left. Nevertheless, the integrity of the solution is only as good as the atmosphere of NO above it, which is why Shaw and Vosper specify a high excess of NO. Losses of NO in the atmosphere will drive Equation (2) forward, converting the blue-green N_2O_3 solution to yellow dinitrogen tetroxide (N_2O_4). Higher temperatures also drive the reaction forward. In many solvents, a 1 atm partial pressure is sufficient to maintain a concentration of about 1 M N_2O_3 at 0 °C in near purity.

It is thus useful to think of N_2O_3 solutions the way one thinks of carbonated beverages, which maintain their concentration of carbonic acid so long as they are capped. When opened, this carbonic acid will steadily convert back to carbon dioxide and bubble out, gradually causing the beverage to go “flat”. Like carbonated water, organic N_2O_3 solutions takes some time to degas, and a beaker of blue solution can be kept in the open air for several minutes before losing considerable amounts of N_2O_3. Table 1 lists four typical solvents and the measured degassing rate from a surface area of 1 cm^2 (for a vessel of 2.7 mL volume, kept inside a 4 L container in between tests to limit water absorption and air circulation). Thus a solution in toluene left without agitation at room temperature and protected from air currents will have approximately 1/2 of its starting N_2O_3 concentration after 2.6 hours.

Table 1. Rate of dinitrogen trioxide loss from a still solution.[a]

Solvent	k_{loss} [s^{-1}]	$\tau_{1/2}$ [h]
Acetonitrile	1.9×10^{-4}	1.5
Dichloromethane	3.8×10^{-4}	0.8
Toluene	7.3×10^{-5}	3.8
Chlorobenzene	5.2×10^{-5}	5.3

[a] 1 cm^2 surface at 25 °C. Estimated errors are in the last digit.

It is thus preferable to work with dinitrogen trioxide solutions in a “one-pot” manner, in which the solution is first formed and further reactants are then added to the same vessel. Transfer of the dinitrogen trioxide solutions into an atmosphere that is not already suffused with NO gas will cause some dinitrogen trioxide degradation as the more volatile NO component is driven out of solution.

The capacity of various solvents to maintain the N_2O_3/NO–NO_2 equilibrium varies with their polarity (greater polarity allows greater N_2O_3 content) and with the electron donating character of the aromatic ring in aromatic solvents. Other factors such as viscosity and boiling point can make a difference, but the electronic character predominates, as it stabilizes the N–N bond and prevents the N_2O_3 from dissociating. Table 2 lists some common solvents and the concentration of N_2O_3 that may be achieved in them through the dynamic absorption method under the conditions described below (the balance of the mol-% will be N_2O_4, which is also stabilized by these solvents[10]).

Based on our titration experiments, we find that our system of absorbing NO directly into the solvent system allows for far higher concentrations to be formed and maintained than what Vosper initially reported, even at elevated temperatures. In his research, Vosper attempted to prepare N_2O_3 by absorbing NO gas directly into liquid N_2O_4, with violent agitation and without another stabilizing solvent. With this method at –5 °C the maximum N_2O_3 concentration was 54 %.[8] Furthermore, it was concluded that at 0 °C it was impractical to maintain an N_2O_3/N_2O_4 solution beyond around a 60:40 ratio[12] In this case it was prepared pure at –78 °C and then warmed with concentrations being, based on the UV/Vis spectrum, which has significant overlap between the two compounds. We believe that our measurement method is more robust and reflects the true potential concentrations.

We confirm prior results that almost any solvent that is either (a) polar and/or (b) aromatic can serve to stabilize N_2O_3, with the exception of protic solvents such as water or alcohol, which react with it. Our laboratory has thus far worked with stable solutions in acetic anhydride, acetone, acetonitrile, benzaldehyde, benzene, chlorobenzene, chloroform, dichloromethane, dimethyl sulfoxide, ethyl acetate, mesitylene, 1,1,2,2-tetrachloroethane, tetrahydrofuran, toluene, and xylene. It is possible to form a solution in anisole, but reaction with the solvent is apparent within an hour; benzaldehyde will also react (forming benzoic acid), though over a span of days.

The exact mechanism(s) for the stabilization in these solutions remains speculative. Prior workers have proposed that the stabilizing mechanism in aromatic solvents was due to a charge transfer interaction.[13] Low temperature studies of N_2O_4 dis-

Table 2. N_2O_3 content of solutions prepared by dynamic absorption.

Solvent	mol-% N_2O_3 (0 °C)	mol-% N_2O_3 (25 °C)	ε (25 °C) [L/cm mol]	ε (0 °C)[a] [L/cm mol]
Acetonitrile	91.7(6)	73.6(5)	9.8(7)	10.7
Dichloromethane	76.8(5)	59.1(4)	8.5(7)	9.2
Chlorobenzene	91.5(7)	55.7(4)	10.9(9)	15.2
Benzene	88.7(4)	66.5(3)	14.0(8)	16.3
Toluene	99.8(7)	69.0(3)	15.3(7)	18.7
Xylene	98.5(8)	69.0(5)	17.4(8)	20.3
Mesitylene	100.7(7)	71.1(5)	16.4(8)	20.8

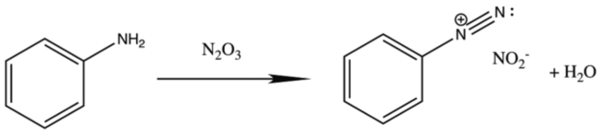
[a] ε values taken from Shaw and Vosper,[11] which were determined at lower temperatures. These values were not found to hold at 25 °C and were thus recalculated, but are accurate up to 0 °C.

solved in benzene[14] have shown that orbital overlap between the dinitrogen tetroxide and the aromatic rings produces a kind of sandwich compound, so it is probable that a similar interaction goes on in N_2O_3 (although the color change of N_2O_4 in aromatic solvents[10] can be more pronounced than what is seen in N_2O_3). Polar solvents stabilize N_2O_3 as well, but to a lesser degree; this is likely because this environment favors the more polar N_2O_3 molecule (2.572 D[15]) over its less polar substituents (NO_2 0.289 D;[16] NO 0.160 D[17]), making it the enthalpically favored form.

Three Examples of Anhydrous N_2O_3 Chemistry

As reported,[18] Primary and secondary amines[18] react with N_2O_3 solutions similar to nitrous acid, an unsurprising fact given that N_2O_3 is believed to be the reactive form of $HONO_2$, behaving as an [NO^+] donor. In general, any system in which protons may be transferred to N_2O_3 can be considered analogous to nitrous acid,[19] so it is in its aprotic reactions under anhydrous conditions that the chemistry of N_2O_3 solutions becomes unique. The transition from aqueous to non-aqueous solvents opens up some interesting possibilities; reactions that normally make use of HNO_2 can be conducted in water-immiscible solvents to improve separation, or even to allow for the isolation of hydrolytically sensitive products that would otherwise be destroyed in water. Three laboratory preparations for which an N_2O_3 preparation offers advantages over nitrous acid are shown in Equations (3), (4), and (5) and are detailed in the Experimental Section.

Diazonium cations are often intermediates in aromatic substitution chemistry and are seldom isolated. However under certain conditions with the inert anions such as tetrafluoroborate stable salts are accessible after metathesis. Unfortunately the nitrite/nitrate salts of benzenediazonium, for example, are notoriously unstable[20] and must usually be prepared with special measures in place to remove excess nitrous acid. We find however these salts can rapidly be prepared in high yield and purity using anhydrous N_2O_3 system, Equation (3), from an acetonitrile/benzene solution. The off white salts can be filtered and used as is or recrystallized from benzene.



(3)

In the case of nitrosylsulfuric acid, also recognized as chamber crystals from the chamber process, a pure powder preparation is not normally possible except from a fuming HNO_3/SO_2 gas reaction. With dinitrogen trioxide it can be prepared directly from laboratory grade sulfuric acid in acetonitrile [Equation (4)]. The nitrosylsulfuric acid product is a fluffy white solid which can be isolated and used at this stage or recrystallized from acetonitrile/dichloromethane.

$$H_2SO_4 + N_2O_3 \longrightarrow ON\text{-}OSO_3H + HNO_2 \tag{4}$$

Finally nitrosyl chloride can also be prepared by treating anhydrous N_2O_3 with concentrated HCl [Equation (5)]. In this case the preferred solvent system employed should be immiscible with water and the product appears after twenty minutes as a brown-orange suspension. The product is readily isolated by passing a stream of nitrogen through the solution and condensing the nitrosyl chloride as a bright orange solid with a liquid nitrogen cold trap. This use of a reagent in a biphasic reaction minimizes the amount of hydrolysis of the product and gives a 45 % yield for the crude and 25 % yield for the final purified product.

$$HCl + N_2O_3 \longrightarrow NOCl + HNO_2 \tag{5}$$

Conclusion

Though considered a laboratory curiosity and infrequently studied in the past century, N_2O_3 is an important nitrogen oxide that plays a role as an intermediate in many nitrogen reactions. By stabilizing and concentrating this intermediate under normal laboratory conditions, we can transform an esoteric substance into a common laboratory reagent, allowing both an easier study of its chemistry and access to useful processes. Merely by eliminating water as the solvent in standard nitrous acid reactions, we can more easily produce and isolate pure nitrosation products. More exotic chemistry also becomes possible by reaction with aprotic systems and by the movement into a new temperature regime (from extreme cold, where most N_2O_3 chemistry is performed, to room temperature and beyond). It is our hope that N_2O_3 will come to be regarded as a useful reagent and that these solutions will become a part of the chemist's expanded toolbox. Future publications will report on the novel chemistry that is possible by treating tertiary amines with anhydrous N_2O_3 solutions.

Experimental Section

Preparation of N_2O_3 Solutions

A sealed 50 mL Schlenk flask equipped with a stir bar is evacuated under high vacuum. It is then flushed with nitric oxide gas. Between 10 and 25 mL of the chosen solvent is then injected with a syringe. Alternatively, solvent can be added first, then freeze-thaw-degassed or sparged with argon, and then finally flushed with NO (if it is not necessary to know the precise quantity of N_2O_3 being produced, the flask with a dry solvent can simply be flushed with NO gas; residual oxygen will result in a small amount of extra N_2O_3 being produced, but this will be inconsequential for many experiments). The flask with its solvent and NO atmosphere is then immersed in an ice-water bath and cooled to 0 °C. A measured amount of oxygen gas is then injected in increments of ca. 10 mL with a gas tight syringe. Each O_2 addition is followed by allowing the mixture to stir gently for ca. 5 min while under a weak positive pressure of NO gas (ca. 0.7 kPa above atmospheric pressure), after which the next dose of O_2 may be added. NO and O_2 combine to form NO_2, which consumes another NO to make N_2O_3, which dissolves in solution. Note that each mol of O_2 forms two mol of N_2O_3.

The resulting solution of N_2O_3, when kept at this temperature or below and with an atmosphere of NO over top of it, will keep indefinitely, though in practice it is best to use it immediately. Long term storage requires the use of glass stoppers, as rubber septa are destroyed by the gas over a span of hours. The addition of liquids to nitrogen trioxide solutions is best performed with a syringe through a septum while the reaction vessel is allowed to vent to a gas bubbler or a gas collection vessel, as gaseous byproducts are common. For precise measurements, added reactants should be cooled in the appropriate medium before addition to a cooled trioxide solution; failure to chill prior to addition can cause some nitric oxide/nitrogen dioxide to boil out of solution (cold solutions must be added promptly as pipette tips/syringe needles can condense atmospheric water during transfer). Solids can be added quickly by means of a solid addition funnel, and the vessel closed immediately afterwards.

Determination of N_2O_3 Concentration: In order to arrive at the values given in Table 2, the precise quantities of N_2O_3 in solution were determined by titration with oxygen gas, which converts it to N_2O_4, in the following manner: 10 mL of N_2O_3 solution was prepared according to the dynamic absorption method described above, at 0 °C using 10 mL of solvent and 30 mL of oxygen gas. Once NO absorption was complete, the atmosphere inside the solvent vessel was flushed out with a flow of argon (ca. 2–3 seconds of strong flow, such that no new NO_2 was seen to form when the O_2 is added). O_2 titration was carried out by adding the gas incrementally with a gas tight syringe (first by 10 mL, scaling down to 0.25 mL as the blue-green coloration vanished, which signaled an approaching endpoint). At very low concentrations of N_2O_3, dissociation of NO into the headspace "hides" the remaining NO, so the vessel was cooled in an ethanol/dry ice bath, which immediately converts it back to visible N_2O_3. It was then warmed for 10 min and titration was continued. When no blue-green was visible at –78 °C, the final endpoint was determined by the UV/Vis absorption in the 660–720 nm region[21] (the peak position for residual N_2O_3 can vary dramatically with the solvent used). It was compared to an N_2O_4 solution at the same temperature (N_2O_4 has a faint, broad absorption in this region and replaces the baseline). It has previously been established by spectroscopic[12] and Evans-method NMR[19] techniques that the N_2O_3 in solution is ca. 99 % in the covalent form, rather than dissociated into $[NO^+][NO_2^-]$ or $[NO][NO_2]$.

Synthesis of Benzenediazonium Nitrite

A mixture of 5 mL of acetonitrile and 10 mL of benzene is cooled to 0 °C on an ice bath, and a 0.146 M solution of N_2O_3 is prepared in it, as above, inside a 50 mL three necked flask. 0.1 mL of aniline (distilled and recrystallized from ether at –20 °C, and stored over molecular sieves) is diluted in 5 mL of benzene, and this solution is added by pipette (at a rate of ca. 1 mL over 3 seconds) to the mixture while the liquid is stirred smoothly and briskly. The blue of the reaction mixture will disappear once the N_2O_3 is fully consumed, and the solution becomes faintly yellow. Stirring is halted and the white-to-yellow precipitate is allowed to form for 5 min. It is then filtered by gravity on filter paper (see below), and washed with cold benzene, then air dried (or vacuum dried on an open watch glass) to yield glossy, off-white flakes of benzenediazonium nitrite, pure by IR and NMR spectroscopy. The filtrate can be saved and a second and sometimes third crop of product may form on cooling. Yield by weight: 85 %. IR: $\tilde{\nu}$ = 3088, 3064, 3040, 2396 (w), 2296 (w), 1756 (w), 1607, 1551, 1458 (s), 1358 (s), 1318 (s), 1310 (s), 1160, 1092, 830, 758 (s), 605 (s), 524 cm^{-1}. NMR: The product reacts slowly with all solvents that it dissolves in; the reaction with methanol was sufficiently slow to perform NMR in CD_3OD: 8.66 (d), 8.306 (t), 8.006 (t). No other impurities were detected, except for a trace of the decay product, which grows in over ca. 24 h as the product disappears.

An excess of N_2O_3 during synthesis will instead tend to produce benzenediazonium nitrate,[22] due to oxidation of the main product. The growth of an IR peak at 1386 cm^{-1} signals its formation. The products are otherwise very similar.

WARNING*: Benzenediazonium nitrite/nitrate is highly explosive and will detonate on warming to 80 °C, from sufficient friction, or from a sharp blow. Synthesis in large quantities is not recommended, and even small quantities should be filtered using gravity and a filter paper; loosen the filtrate before drying. DO NOT allow to dry in a sintered glass frit. It is soluble in H_2O, EtOH, and MeOH.*

Following a literature technique,[23] we attempted to ascertain the purity of our product by means of chemical activity. The product was treated with sodium thiosulfate in water, and the excess thiosulfate was titrated with an iodide/I_2 solution, using a starch indicator. The product reacts readily with thiosulfate in a 1:2 ratio to yield an orange solution containing a range of aromatic products. As determined by this method, the yield, in terms of functional benzenediazonium from initial aniline reactant, is 76 %, which compares well to the by-weight yield.

Synthesis of Nitrosyl Chloride: One mL of concentrated aqueous hydrochloric acid (36.5 %) is added to an equimolar dinitrogen trioxide solution (20 mL at 0.5 M). In water immiscible solvents (i.e. toluene, dichloromethane), 20 min of stirring allows for the formation of a cloudy yellow-brown solution; in acetonitrile, the solution immediately becomes a clear red-orange. In any of these solutions the main product is seen to be the same. Bubbling nitrogen gas through the solution for 60 min and collecting the stream in a liquid nitrogen cold trap gives nitrosyl chloride as a brilliant orange solid. The functional yield in situ from an acetonitrile preparation was determined to be 45 % by reacting the product with mercaptoethanol and measuring the UV absorbance of the resulting nitrosothiol (ε = 34.3 at 548 nm), assuming a 1:1 formation of nitrosothiol from each nitrosyl chloride (thiols are extremely reactive with nitrosating agents, while NOCl is unlikely to react with the ethanol component[24]). Collected as a pure product in a cold trap, a 25 % yield (based on the added HCl) can be recovered. Nitrosyl chloride evaporates quickly at room temperature, but can be identified by the UV spectrum of its vapor.[25] UV/Vis: ε_{max} at about 220 nm, 341 nm, smaller peaks at 435 nm, 474 nm.

Synthesis of Nitrosylsulfuric Acid: Sulfuric acid (0.5 mL) is introduced to excess dinitrogen trioxide in acetonitrile (30 mL of 0.5 M solution) to yield a white product which forms as dry granules. The product will spontaneously decay to nitric oxide and sulfuric acid if removed from the solvent. Instead, the product is washed three times with cold dry acetonitrile, then dried under vacuum to yield nitrosylsulfuric acid[26] (chamber crystals) in 78 % yield as a fluffy white powder. Alternatively, washing with acetonitrile then stirring with dry dichloromethane for 24 h will yield dense white chunks of dry precipitate, in similar yield. The reaction can be performed in other non-aromatic solvents such as dichloromethane, where it forms as an oily paste that requires more drying. The final product in any case decays in air with release of nitric oxide, and reacts violently with water and alcohol, again releasing nitric oxide. IR: $\tilde{\nu}$ = 3470 (br), 1656 (w), 1438, 1383, 1363, 1268, 1156 (str), 831 cm^{-1}. Confirmed by comparison with product prepared by literature techniques[27] (absorption of NO gas into sulfuric acid), which produces the 40 % by weight solutions (in sulfuric acid) normally sold commercially.

Nitrosylsulfuric acid can be prepared in aromatic solvents, but this produces intensely colored side products (red and orange) from reaction with the solvent. In benzene the reaction is relatively clean and this solvent may be used for the synthesis if necessary, though the level of purity has not been ascertained. CAUTION: Use of mesitylene as a solvent will produce a violent chain reaction, and should be avoided.

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Keywords: Nitrogen · Diazo compounds · Nitrosation · Nitration · Acidity

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