

## Chemistry of Nitrogen Oxides

## Isolable Adducts of Tertiary Amines and Dinitrogen Trioxide

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**Abstract:** Anhydrous dinitrogen trioxide, N<sub>2</sub>O<sub>3</sub>, dissolved in toluene or dichloromethane rapidly forms stable adducts with tertiary amines such as triethyl-, tribenzyl-, or trihexyl-amine. With DABCO, 1,4-diazabicyclo[2.2.2]octane it forms a free flowing orange solid. The analytical and spectroscopic data for the DABCO adduct indicate a formula of DABCO(N<sub>2</sub>O<sub>3</sub>)<sub>2</sub> which has been characterized by IR, Raman, and UV/Vis spectroscopy. The R<sub>3</sub>N-N<sub>2</sub>O<sub>3</sub> adducts are hydrolytically sensitive oils or solids which rapidly react quantitatively with thiols to give RSNO. The reac-

tivity of the amine adducts is variable, and the products include amine N-oxides, ammonium nitrites, and ammonium nitrates depending upon the adduct, conditions, and substrate. Density functional theory, B3LYP/aug-cc-pvtz, has been used to compare the predicted structures and spectroscopic data for mono and bis adducts. Geometry optimization of the R<sub>3</sub>N-N<sub>2</sub>O<sub>3</sub> adduct gives a weakly bound Lewis acid/base adduct with the amine nitrogen closest to the nitrosyl N with a strongly tilted planar ONNO<sub>2</sub> unit.

## Introduction

A common misconception in organic chemistry textbooks of the mid 1900's was that tertiary amines can be distinguished from primary or secondary by the fact that they do not react with nitrous acid.<sup>[1]</sup> In their exactly precise examination of this reaction Smith and Loeppky<sup>[2]</sup> stated in 1967 that this is a "most persistent myth in organic chemistry, notwithstanding a veritable parade of experimental refutations extending over a century". Nevertheless, the myth persists.<sup>[3]</sup> The reaction between tertiary amines and nitrous acid is slow, requiring many hours at 0 °C and several hours at ambient temperature, but it proceeds nonetheless. Smith and Loeppky proposed a nitrosative cleavage as the most likely mechanism, Figure 1.

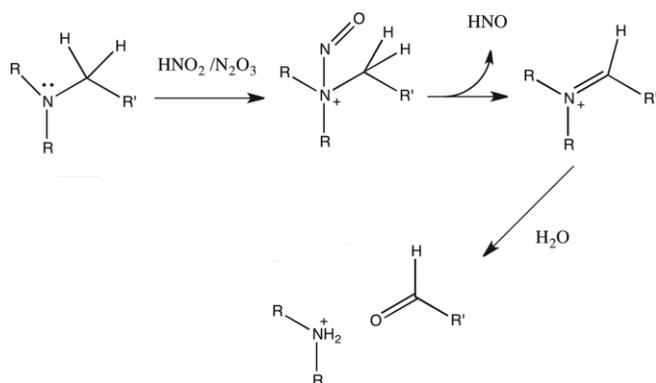


Figure 1. Smith and Loeppky's nitrosative cleavage of tertiary amines.

We have recently developed a useful procedure for the preparation of dinitrogen trioxide in anhydrous organic solvents and

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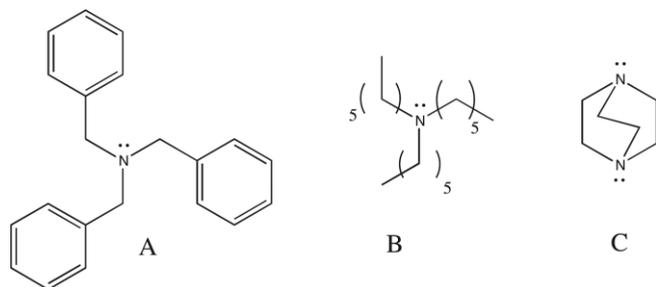
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <https://doi.org/10.1002/ejic.201800654>.

demonstrated the unique nitrosations possible with this reagent.<sup>[4]</sup> Dinitrogen trioxide, N<sub>2</sub>O<sub>3</sub>, the anhydride of nitrous acid, exhibits very similar chemistry to its hydrate. Indeed, N<sub>2</sub>O<sub>3</sub> may be the active form of nitrous acid,<sup>[5]</sup> formally behaving as [NO<sup>+</sup>][NO<sub>2</sub><sup>-</sup>]. The obvious difference between them is that, in an organic solution of pure N<sub>2</sub>O<sub>3</sub>, one has neither water nor protons available unless they are supplied by the other reactants. Thus stabilized, N<sub>2</sub>O<sub>3</sub> reacts with primary and secondary amines in a fashion very similar to nitrous acid. However, for tertiary amines we see an important difference compared to what Smith and Loeppky described: these reactions proceed immediately, retain the N-N bond, and lead to N<sub>2</sub>O<sub>3</sub> adducts of varying stability. In the case of aqueous nitrous acid transformations, the N<sub>2</sub>O<sub>3</sub> adduct would be rapidly hydrolyzed. We report however that one of these, 1,4-diazabicyclo[2.2.2]octane, DABCO, forms an amine adduct with sufficient stability to be isolated and bottled as a semi-stable solid N<sub>2</sub>O<sub>3</sub> source. In this paper we describe the preparation and the characterization of this compound. In addition, the products of dinitrogen trioxide addition to triethylamine, trihexylamine, triphenylamine, tribenzylamine, and triphenylphosphine are described. Together these results lay the ground work for developing new, more efficient nitration reagents and conditions.

## Discussion

The rapid rate of reaction between solutions of dinitrogen trioxide and tertiary amines is initially surprising, given the accepted lore concerning the reaction of nitrous acid with tertiary amines. Certainly part of the relative sluggishness of the nitrous acid reaction is due to the unfavorable dehydration equilibrium, Equation (1), which leads to low steady state concentrations of aqueous dinitrogen trioxide. Equally important is that the amine inhibits the reaction by lifting the pH. But what becomes apparent upon examination of the different reactions is that

the anhydrous environments used to prepare  $N_2O_3$  also stabilize the products. Thus the use of anhydrous  $N_2O_3$  under these conditions allows for the rapid preparation and isolation of hitherto unknown products in this chemistry. Tertiary amines react rapidly with anhydrous dinitrogen trioxide, but not necessarily in an irreversible way. Certain amines, Scheme 1, allow for the initial adducts to be isolated and characterized.



Scheme 1. Some tertiary amines used to probe the  $N_2O_3$  reaction. A) Tri-benzylamine. B) Trihexylamine. C) 1,4-diazabicyclo[2.2.2]octane (DABCO).

The best example is the adduct formed by DABCO. Stoichiometric mixtures of  $N_2O_3$  and DABCO produce a black solution and a yellow gum. However, higher ratios of  $N_2O_3$  favors precipitation as a free flowing solid, and above a ratio of 2:1  $N_2O_3$ /DABCO the product will begin to spontaneously precipitate as a loose powder. The best yield was found at an 8:1 ratio. This air-sensitive solid is a vividly orange powder, which is relatively stable under inert atmosphere. In a tightly closed vial a slight positive pressure of nitric oxide will develop over a period of days. Gravimetrically the addition of dinitrogen trioxide to DABCO corresponds to a marked increase in mass by a factor of 1.88, or by 94 % yield for the bis( $N_2O_3$ ) adduct of DABCO. While performing combustion analysis for this temperature and water sensitive product requires attention to detail, the values obtained correspond to the bis adduct,  $DABCO(N_2O_3)_2$ , with a minor amount of the mono adduct,  $DABCO(N_2O_3)$ . For these solids a strong, conspicuous band appears in the IR spectrum at  $1896\text{ cm}^{-1}$  (Figure 2), in addition to numerous other  $N_2O_3$  framework and DABCO bands. A new band is also found in the Raman, at  $1908\text{ cm}^{-1}$ . The IR spectrum needs to be measured in a protective inert mull as the DABCO adduct will react with KBr or atmospheric moisture. For comparison the typical IR active  $\nu(\text{NO})$  bands in this region are  $\approx 2377\text{ cm}^{-1}$  for nitrosonium  $[\text{NO}^+]$ ,<sup>[6]</sup>  $\approx 1875\text{ cm}^{-1}$  for NO, and  $\approx 1470\text{ cm}^{-1}$  for  $\text{NO}^-$ .<sup>[7]</sup> In the gas phase  $N_2O_3$  itself has a peak at  $1840\text{ cm}^{-1}$ . While the observed band at  $1896\text{ cm}^{-1}$  in the DABCO adduct band is dominated by the  $\nu(\text{NO})$  character, and it is tempting to interpret this solely in terms of its  $\nu(\text{NO})$  character, the normal coordinates also reflect the degree of coupling of the terminal ON to the remaining  $\text{NO}_2$  framework. For example, although these values suggest that there is relatively little nitrosonium character in  $N_2O_3$  in the gas phase, and that base addition enhances or stabilizes the formal charge separation, this interpretation does not hold up against the theoretical results described below.

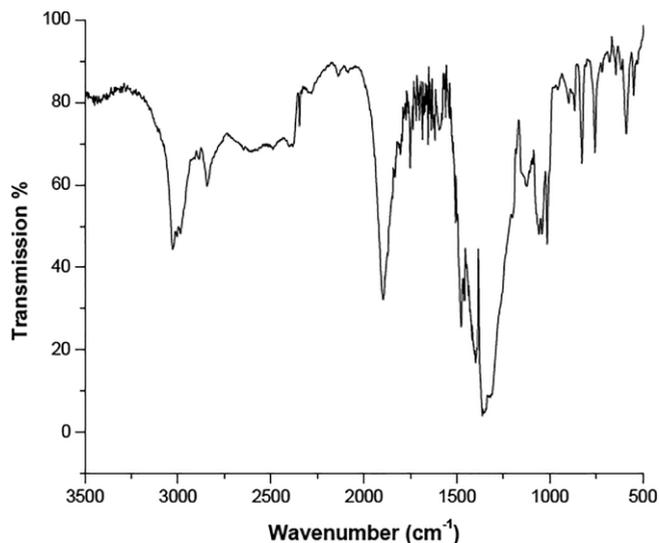


Figure 2. Difference IR spectrum of a hexachlorobutadiene mull of the DABCO adduct with two  $N_2O_3$  as an orange powder.

When exposed to moist air, the powder will lose approximately 18 % of its mass and bleach white, releasing a gas in the process and losing the  $1898\text{ cm}^{-1}$  peak. The resulting white product is the protonated nitrate salt of DABCO.

The orange  $DABCO(N_2O_3)_2$  adduct reacts as a nitrosonium donor: with thiols such as benzyl mercaptan, mercaptoethanol, or glutathione, thionitrites ( $\text{RSNO}$ ) form instantly [Equation (2)].



For the DABCO bis adduct the net nitrosylation corresponds to 89 % yield by a two-equivalent reagent. Many solid substrates treated with dinitrogen trioxide often have residual  $N_2O_3$  adhering to them. For example, although the final isolated salts are often colorless free flowing powders, immediately after the preparation they can remain green for hours or days afterwards. Thus adduct formation and surface adhesion is general characteristic of dinitrogen trioxide. In contrast however, the thionitrosyls which result from the reaction of  $\text{R}_3\text{N}-N_2O_3$  and mercaptans none of the products appear to retain adducted dinitrogen trioxide. The initial and subsequent products have UV spectra which correspond to complete initial nitrosation with little surface adhesion or decomposition to the salt by product.<sup>[8]</sup>

$DABCO(N_2O_3)_2$  is somewhat soluble in warm dichloromethane or chloroform; DMSO will also dissolve it to make a blue-green solution.  $N_2O_3$  on its own in DMSO is navy blue but slowly reacts with the solvent. In DMSO both the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR show a single peak downshifted from the DABCO peaks, proving that the cyclized structure has neither opened, nor is it mono-substituted on the NMR exchange timescale. Addition of more DABCO to this mixture will not show a second peak, however, but will produce a fast exchange average that broadens at lower temperature. The colorless nitrate salt of DABCO is poorly soluble in organic solutions, but also shows a single sharp peak in the  $^1\text{H}$  NMR at room temperature.

Taken together, these data demonstrate that DABCO interacts with dinitrogen trioxide to form a bisadduct,  $[\text{N}_2\text{O}_3]\text{-N}(\text{C}_2\text{H}_4)_3\text{N-}[\text{N}_2\text{O}_3]$ . In the absence of suitable X-ray diffraction grade crystals, the detailed solid-state structure remains and analytically and spectroscopically defined and theoretically modeled. Density functional theory at the B3LYP/aug-cc-pvtz level yield local ground state minima for the bis and mono adducts shown in Figure 3 as well as in the supplementary data. Key predicted structural and spectroscopic data are summarized in Table 1 with the adducts contrasted with the gas phase microwave structure of  $\text{N}_2\text{O}_3$ .<sup>[9]</sup> Dinitrogen trioxide binds as an asymmetrical Lewis acid to DABCO with the “nitrosonium” nitrogen closest to the Lewis base nitrogen and the planes of the dinitrogen trioxides twisted  $9^\circ$  away from an orthogonal orientation. Electron donation by the base significantly lengthens all bonds in the  $\text{N}_2\text{O}_3$  fragment and the net ensemble has long N–N bonds both within the nitrogen oxide, and to the base,  $\text{R}_3\text{N-N}(\text{O})\text{NO}_2$ . The calculated and experimental IR data for the  $[\text{ONNO}_2]$  bands suggest relatively weak coupling across the DABCO. Thus the  $\nu(\text{NO})$  band is split into asymmetric and symmetric modes. Both bands are predicted to have significant oscillator strengths and theoretically differ by  $14.4\text{ cm}^{-1}$ . Experimentally only a single intense albeit broadened band is observed in this region and support the proposed weakly coupled bis adduct with only one broad “nitrosonium” like stretch.

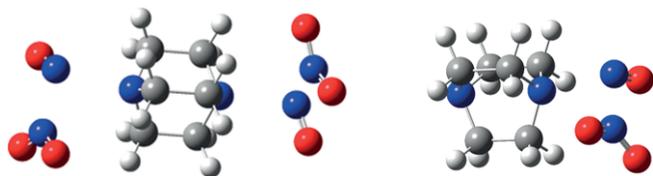


Figure 3. Calculated structures, B3LYP/aug-cc-pvtz, of the ground state of the  $\text{N}_2\text{O}_3/\text{DABCO}$  adducts. Left-bis, right-mono adducts.

Table 1, and Figure 4, collect the important bond lengths, as well as the calculated absorption wavelengths and oscillator strengths.

The agreement between the calculated and the observed IR spectra is nevertheless excellent and the calculated models need to be carefully considered. The  $\text{N}_2\text{O}_3$  molecule is thus predicted to be little altered in the formation of the complex, with only a slight lengthening of the N–N bond, in agreement with

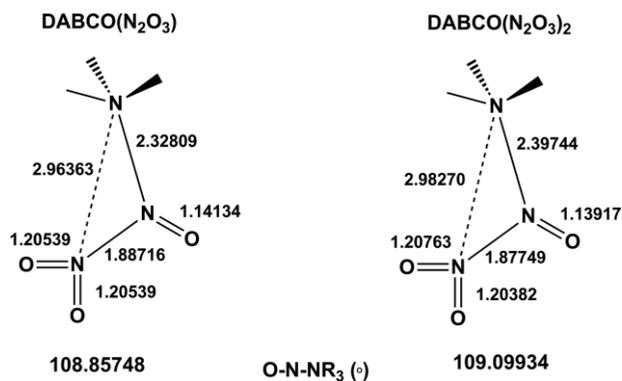


Figure 4. Optimized geometries, in  $^\circ$  and  $\text{Å}$ , for mono and bis  $\text{N}_2\text{O}_3$  adducts of DABCO. For the bis adduct averaged values of the two  $\text{N}_2\text{O}_3$  are given.

the modest shifts in the IR spectrum. The intense oscillator strength predicted for the second excited state of the *mono* product fits with the observed initial reaction when a small amount of DABCO is added to an  $\text{N}_2\text{O}_3$  solution in excess: the solution becomes a dark red-brown liquid. Attempts to study the dark solution are frustrated by the insolubility of the DABCO adducts, their air sensitivity, their precipitation when the atmosphere changes, and their proclivity to spontaneously yield yellowed DABCO when warmed. Careful dilution and transfer into a short path length cell enabled a UV/Vis spectrum to be taken, in which it could be seen that the color stems from a broad peak that extends over the 300–400 nm range, as well as from a long tail that reaches throughout the visible range. This fits the general pattern of the *mono* adduct absorbing strongly in the violet region (appearing red), where the bis *adduct* red shifts into blue absorption, becoming more yellow-orange.

The hydrolysis of  $\text{DABCO}(\text{N}_2\text{O}_3)_2$  proceeds with a nitrogen disproportionation so that formation of a bis  $\text{HNO}_3$  salt, (Figure 5) must be formally accompanied by  $\text{N}^{\text{I}}$  or  $\text{N}^{\text{II}}$  derivative(s). The corresponding reduction partner might include  $\text{HNO}$ , but, if formed, this is expected to rapidly dimerize to give nitrous oxide. Yet no  $\text{N}_2\text{O}$  was detected among the gaseous products. There is also no indication that  $\text{NO}$  gas forms during this hydrolysis as judged by its characteristic reaction with dioxygen. Dinitrogen tetroxide is also known to form amine adducts of this kind,<sup>[10–13]</sup> but this is the first reported instance that we are aware of for a dinitrogen trioxide adduct. Theoretically, BLYP/

Table 1. Contrast in experimental and DFT calculated Mono- and bis-DABCO/ $\text{N}_2\text{O}_3$  adduct data.

Structure	Bond Lengths [ $\text{Å}$ ]			IR $\nu(\text{NO})^{[\text{b}]}$	Electronic Spectra		Electronic Spectra			
	$\text{R}_3\text{-N}$	$\text{ON-NO}_2$	$\text{O-NNO}_2$		$s_1^{[\text{a}]}$ $\lambda_1$	$f_1$	$s_2$ $\lambda_2$	$f_2$	$s_3$ $\lambda_3$	$f_3$
Gas phase free molecule										
$\text{N}_2\text{O}_3$ [g] (theory)	–	1.8691	1.1309	1930.2	828	0.0002	331	0.0000	313	0.0001
$\text{N}_2\text{O}_3$ (exp.)		1.864	1.1309	1840	700 nm <sup>[c]</sup> , 15.3 $\text{cm}^{-1}$ , $\text{M}^{-1}$					
Amine Adducts										
mono	2.2931	1.8971	1.1449	1837.1	528	0.0014	406	0.1463	332	0.0004
bis	2.3562	1.8896	1.1420	1849.6	586	0.0013	536	0.0013	413	0.0701
Bis Adduct (exp.)	–	–	–	1855.2 1896.9	–	–	–	–	–	–

[a]  $s_n$  denotes the excited state. Wavelengths given in nm.  $f_n$  Denotes the oscillator strength. [b] Mode in  $\text{cm}^{-1}$ . [c] Observed  $\lambda_{\text{max}}$  and extinction coefficient.<sup>[4]</sup>

aug-cc/pvtz, both DABCO and trimethylamine form weakly bound adducts with  $N_2O_4$ . As shown in the supplementary data, these adducts have long  $R_3N-NO_2(NO_2)$  interactions averaging 2.94 Å. Sisler noted that the adducts of tertiary amines were only isolable at  $-70\text{ }^\circ\text{C}$  but rapidly decomposed on warming to  $0\text{ }^\circ\text{C}$  whereupon rapid decomposition set in.

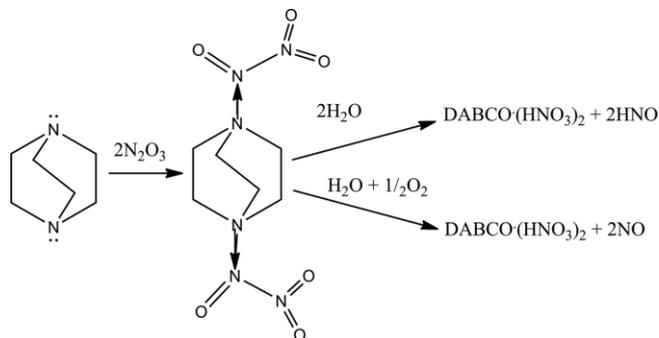


Figure 5. Formation and proposed decay of the DABCO/ $N_2O_3$  adduct.

With the exception of triphenylamine (which undergoes *para* nitration of the phenyl ring), the other tertiary amines react with  $N_2O_3$  in the same mode as DABCO, but none of the adducts have the same stability. Both tribenzylamine and trihexylamine will react with  $N_2O_3$  to give a yellow oil, which readily hydrolyzes in air to produce tribenzylammonium nitrate and trihexylamine *N*-oxide, respectively. The trihexylamine product is deep orange when  $N_2O_3$  is in four fold excess, but otherwise forms a plum purple color. Either form reacts with mercaptans to produce nitrosothiols, as the DABCO product does, albeit only in a 30 % yield; this suggests that it too is an  $N_2O_3$  adduct, yet in the IR we find no peak in the  $\approx 1800\text{ cm}^{-1}$  region. There is a weak peak at  $1671\text{ cm}^{-1}$  that collapses into  $1700\text{ cm}^{-1}$  immediately upon exposure to air, which could be an NO moiety with more nitroxyl character. Tellingly, this oil can be dried thoroughly in vacuo until the mass ceases to fall, but it will then lose mass ( $\approx 4\%$ ) in the first few minutes of air exposure.

The tribenzylamine product, has conspicuous adduct peaks in the IR spectra, strongly at  $1656\text{ cm}^{-1}$ , and weakly at  $1744$  and  $1712\text{ cm}^{-1}$ . These bands vanish when exposed to air. Yet this compound does not produce nitrosothiol when exposed to mercaptans but instead results in a new, unidentified compound. It appears that both tribenzyl and trihexylamine interact with and may even carry  $N_2O_3$ , but are more capable of donating electron density to the  $N_2O_3$  and are thus more prone to decay pathways other than  $NO^+$  production.

Exceptionally, trihexylamine decays to its *N*-oxide, rather than the ammonium nitrate form seen for tribenzylamine and DABCO. There is a significant difference in basicity for trihexylamine, and perhaps this plays a role. A comparison to triphenylphosphine may be instructive: the phosphine has a high affinity for oxygen, which it gathers from  $N_2O_3$ , releasing two NO in the process. Thus  $N_2O_3$  can act as a single oxygen atom transfer agent: for example,  $N_2O_3$  solutions form a transiently stable solution in benzaldehyde, but this is slowly transformed into benzoic acid on standing. When moisture is present during the reaction of triphenylphosphine and dinitrogen trioxide, an interesting side product results (Figure 6); a hydrogen bonded adduct between the oxide and nitric acid, first described by Tranter and Addison.<sup>[14]</sup> The ability of the tribenzylamine to donate electron density to the central nitrogen similarly predisposes it to form the *N*-oxide, whereas the less basic amines tend to form  $R_3NH^+$ .

As the less rigid trihexyl and tribenzylamines form products that are less stable than the DABCO complex, so smaller amine adducts like triethylamine are correspondingly even more transient. Triethylamine reacts immediately with  $N_2O_3$  to make a bloom of red color that quickly fades. Most tertiary amines will produce a colored complex at first. This red species can be maintained in a reaction at  $-80\text{ }^\circ\text{C}$ , but all attempts to isolate it at room temperature have failed, the only remnant being a deep red stain in some of the crystalline products. Smith and Loepky also reported the formation of red colored compounds with triethylamine and  $N_2O_3$  at low temperature that vanish on warming; they credited it to the formation of a temporary  $Et_3N-NO^+$  ion. On warming the solution turns green as white precipitate forms. The primary product recovered was identified as triethylammonium nitrite  $[(C_2H_5)_3-NH][NO_2]$  by IR, Mass Spec, and NMR spectroscopy. Curiously, when the product is kept away from air and dissolved in dichloromethane, the UV/Vis peak at  $370\text{ nm}$  does not match that of triethylammonium nitrite which has a  $\lambda_{max}$  at  $320\text{ nm}$  in dichloromethane.

If triethylammonium nitrite is indeed the direct product of the reaction, this implies the presence of moisture in the reaction, but these products form regardless of the precautions taken to work under inert atmosphere. The presence of moisture will lower the yield and form a hygroscopic nitrite salt and cause greater color variation, but under the best conditions around 50 % of the triethylamine is isolated as triethylammonium nitrite. If the product is undergoing nitrosative cleavage (Figure 7), as Smith and Loepky proposed, then this could be

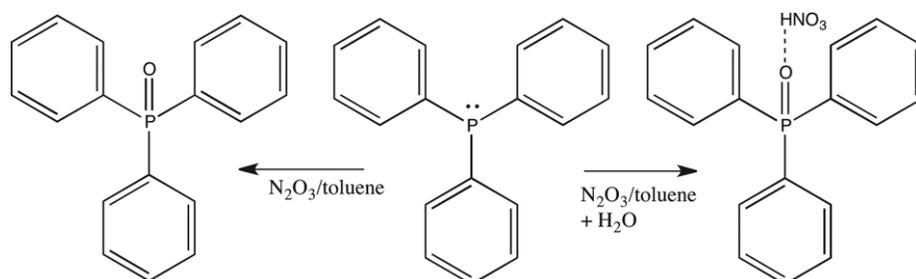


Figure 6. Oxidation of triphenylphosphine to its oxide (left) and Tranter's adduct (right).

the source of the moisture, yet the major products of this would be diethylnitrosamine from the subsequent reaction of the secondary amine with  $N_2O_3$ /nitrous acid. Diethylnitrosamine was only detected in trace amounts.

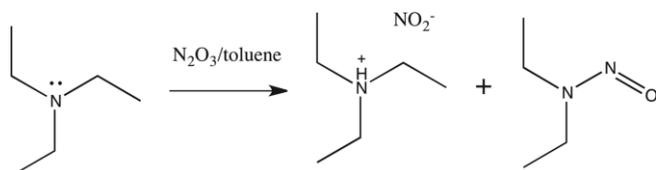
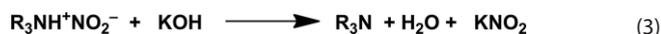


Figure 7. Products of dried triethylamine and dinitrogen trioxide.

The fact that gas evolution is only seen when  $N_2O_3$  is present in excess, and that this correlates with the oxidation of nitrite to nitrate suggests a nitrogen disproportionation reaction to yield  $HNO/N_2O$  gas. From prior reports the cleavage reaction is relatively slow, requiring hours to see any substantial product,<sup>[2]</sup> not the instantaneous release we see within seconds of addition. The recovered triethylammonium salt precipitate can be triturate with alcoholic KOH to produce potassium nitrite, Equation (3):



However, in situ, trituration produces 1.4 equivalents of  $KNO_2$ , suggesting that the  $NO^+$  moiety remains in the solution in some form, perhaps associated with the triethylamine. Assuming it to be an adduct, for example, we see that such a molecule would ideally produce 2 equivalents of  $KNO_2$  by reaction with KOH, Equation (4).



Whatever is occurring afterwards, it is clear that triethylamine does interact with  $N_2O_3$  but does not produce stable  $N_2O_3$  adducts at room temperature.

## Conclusions

The interaction of tertiary amines with  $N_2O_3$  is a general reaction which gives adducts of variable stability and reactivity. This reaction has enormous implications for both biological and synthetic chemistry.  $N_2O_3$  can occur anywhere one finds NO and  $O_2$ , including inside cells,<sup>[15]</sup> and so the possibility that it may form stable adducts becomes biologically relevant. The conditions which stabilize or favor these adducts are particularly within membranes, where [NO] is often higher than in the cytosolic phases. Under these conditions amine  $N_2O_3$  adducts could have longer lifetimes and differing reactivity from free  $N_2O_3$ . For synthetic purposes the stability of the DABCO( $N_2O_3$ )<sub>2</sub> adduct points to potentially useful reagents, ones which might allow for stable solids for stoichiometric nitrosation reactions. Given the recognition that green nitrosation reactions remain a challenge for the chemistry community at large, the isolation and characterization of a stable  $N_2O_3$  adduct points towards future reagents with potentially many applications.

## Experimental Section

The techniques, instruments, and methods used in this research have been detailed in prior publications.<sup>[4]</sup> In addition to the routine use of a 300 MHz NMR spectrometer, in specified cases a 400 MHz NMR spectrometer at 23 °C was used in to acquire some <sup>1</sup>H NMR spectra.

**$N_2O_3$  Solution:** Freshly distilled solvent (toluene/dichloromethane) is poured into a 50 mL three-neck round-bottomed flask and sparged with argon for 10 min and then cooled in an ice bath while under an argon flow. The atmosphere inside the vessel is then flushed with nitric oxide gas (obtained from a Praxair gas cylinder and purified by passage through a 30 cm column packed with KOH and glass wool) at a slight positive pressure ( $\approx 0.7$  kPa above atmospheric). Once the atmosphere inside the vessel is saturated with NO, the gas flow is stopped over a continuously stirred solvent. Up to 10 mL of reagent grade oxygen is then injected through a septum with a gas-tight syringe. The nitric oxide flow is reintroduced, causing the immediate formation of brown vapor and a blue-green solution, and is continued until no brown vapor remains ( $\approx 5$  min). Further  $N_2O_3$  is produced by repeated cycles of this process (each equivalent of  $O_2$  produces two of  $N_2O_3$ , or  $\approx 8.2 \times 10^{-5}$  mol per mL  $O_2$  at STP), as needed. Details of how these solutions are then used in reactions with Lewis bases follow.

**DABCO:** 1,4-Diazabicyclo[2.2.2]octane is purified by sublimation, and 0.025 g is dissolved in 3 mL freshly distilled dichloromethane and added to 10 mL of  $N_2O_3$  dichloromethane solution. This immediately produces a dark color and varying amounts of precipitation, depending on the ratio of  $N_2O_3$  to DABCO used (see Discussion). Use of an 8:1 ratio forms an intensely colored orange precipitate that is recovered by removal of the solvent on a vacuum/inert atmosphere manifold; it is stable when well sealed and/or kept under positive argon pressure. The product is the adduct **1,4-diazabicyclo[2.2.2]octane (bis-dinitrogen trioxide)** ( $[N_2O_3]_2-N(C_2H_4)_3N$  [ $N_2O_3$ ]) in 89 % yield. <sup>1</sup>H NMR ( $CD_2Cl_2$ ):  $\delta = 2.972$  ppm. IR (hexane or Nujol):  $\tilde{\nu} = 3004, 2782, 2585, 2472, 1897, 1474, 1377$  (vs), 1317 (sh), 1184, 1055, 1039, 971, 939, 842, 786, 649, 580  $cm^{-1}$ . Raman: 1908, 1347, 1047, 973, 796, 682  $cm^{-1}$ . Analysis calcd. for a double adduct.  $C_6H_{12}N_6O_6$  (264.20): calcd. C 31.81, H 4.58, N 27.28. Analysis for a single adduct.  $C_6H_{12}N_4O_3$  (188.19): calcd. C 38.29, H 6.43, N 29.77; found C 32.28, H 4.63, N 26.84.

Momentary exposure to atmospheric moisture bleaches the product white, transforming it into **1,4-diazabicyclo[2.2.2]octanium nitrate**  $[HN(C_2H_4)_3NH]^+ [NO_3]^-$  salt, with evolution of nitric oxide gas. IR (Nujol):  $\tilde{\nu} = 3018, 2807, 2617, 2396, 1764$  (w), 1383 (vs, br), 1188, 1040, 891, 851, 823, 803  $cm^{-1}$ .<sup>[16]</sup> This reactivity is partly responsible for our continuing inability to obtain X-ray diffraction data and suitable crystals for single crystal diffraction. Efforts in this regard are ongoing.

Quantification of DABCO( $N_2O_3$ )<sub>2</sub> is readily accomplished gravimetrically or by its reaction with either mercaptoethanol or benzyl mercaptan. Mercaptans react with the base adducts of dinitrogen trioxide to give RSNO and  $[BaseH]^+[NO_2]^-$ .<sup>[4]</sup> Freshly prepared DABCO adduct is dried in vacuo at 0 °C for 1 h and added to an oxygen free aqueous solution of the mercaptan. After 1 min the bright cherry red colored solution is assayed for RSNO concentration at 548 nm,  $\epsilon = 34.3$  L $\cdot$ cm<sup>-1</sup> $\cdot$ mol<sup>-1</sup> for mercaptoethanol, and  $\epsilon = 26$  L $\cdot$ cm<sup>-1</sup> $\cdot$ mol<sup>-1</sup> for benzyl mercaptan.<sup>[17]</sup> A yield of 89 % is calculated on the basis of each molecule formally delivering two equivalents of  $NO^+$  to form nitrosothiol; a control experiment established that the RSNO products react with neither DABCO nor DABCO( $N_2O_3$ )<sub>2</sub>.

**Trihexylamine:** Dropwise addition of 1 mL  $N(C_6H_{13})_3$  diluted in 3 mL of dichloromethane to an equimolar dichloromethane/ $N_2O_3$  solution at 0 °C consumes the blue color before half of the amine is added, with a small amount of nitric oxide gas evolution (<20 mL), forming a yellow solution which becomes pale red-violet within minutes. The solvent is removed under vacuum at 0 °C and the crude product is a deep violet color. UV/Vis ( $CH_2Cl_2$ ): 330 nm (intense), 552 nm (weak). IR (thin film):  $\tilde{\nu}$  = 2960, 2931, 2859, 1671 (w), 1467, 1402, 1378, 1297, 1092, 951, 891, 730  $cm^{-1}$ . Raman: 2879, 1661, 1444, 1341, 1321 (w), 1039, 890, 702.

Exposure of this adduct to the atmosphere for a few minutes produces **trihexylamine N-oxide**<sup>[18]</sup> ( $C_6H_{13})_3NO$  as a yellow oil. Yield (from initial trihexylamine): 94 %. UV/Vis: 330 nm, 370 nm. IR:  $\tilde{\nu}$  = 3447, 2960, 2931, 2859, 1700, 1640, 1467, 1390, 1088, 1020, 730.  $^1H$  NMR:  $\delta$  = 2.905 (t, 6 H), 1.632 (br., 6 H), 1.328 (br., 18 H), 0.902 (t, 9 H)  $cm^{-1}$ .

The use of a four fold excess of trihexylamine with  $N_2O_3$  gives a deep orange colored solution which on concentration results in an orange oil. UV/Vis: 376 nm. The addition of more trihexylamine to this product will reproduce the violet color. Exposure to air will produce a single peak at 348 nm in the UV spectrum. This product is otherwise identical to the product of the 1:1 mixture by IR, Raman, and reactivity.

**Tribenzylamine:** Tribenzylamine, 1 g, is dissolved in 3 mL toluene and added to an equimolar toluene/ $N_2O_3$  solution. After three minutes a white precipitate forms and within 10 min precipitation ceases with a trace of blue remaining in solution. The precipitate is filtered and dried to a snow white powder. Recrystallizing from ethanol gives tribenzylammonium nitrate,  $[(C_6H_5CH_2)_3NH]^+[NO_3]^-$ , 86 %<sup>[19]</sup> confirmed spectroscopically and by X-ray crystallography.  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  = 7.473 (m, 15 H), 4.260 (s, 6 H) ppm.  $^{13}C$  NMR:  $\delta$  = 131.07, 129.97, 129.36, 30.56 ppm. IR:  $\tilde{\nu}$  = 3439 (br., w), 3040 (w), 3000 (w), 2734 (w), 2605 (br., w), 1454, 1390 (vs), 1297 (vs) 1277, 1040, 1016, 911, 758, 698, 501  $cm^{-1}$ .

When the reaction of  $N_2O_3$  and tribenzylamine is performed in dry dichloromethane under nitrogen, a yellow liquid forms without any precipitate. Removing the solvent under vacuum produces a white solid. IR (Nujol mull):  $\tilde{\nu}$  = 2972, 2883, 2847, 1744 (w), 1712 (w), 1656, 1595 (w), 1454 (s), 1378 (s), 1346, 1297 (s), 1040, 1012, 907, 823, 754 (s), 698 (s), 501  $cm^{-1}$ . Exposure of this solution to air leads to tribenzylammonium nitrate. When tribenzylamine is treated with excess  $N_2O_3$  the products include increasing quantities of **benzaldehyde**.

**Triphenylamine:** Triphenylamine, 1 g, is dissolved in 3 mL dichloromethane and added to an equimolar  $N_2O_3$ /dichloromethane solution at 0 °C, which consumes the blue color immediately and produces an intense amber yellow solution. The solvent is removed by evaporation, and the resulting solid is redissolved in a minimum of dichloromethane, diluted in 10-fold hexane, and then chilled to give **(4-nitrophenyl)diphenylamine**  $[(O_2NC_6H_4)(Ph)_2N]$  as orange crystals in 42 % yield.<sup>[20]</sup>  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  = 8.038 (d, 2 H), 7.368 (t, 4 H), 7.193–7.172 (d overlapping t, 6 H), 6.922 (d, 2 H) ppm.  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  = 129.93, 126.52, 125.73, 125.47, 118.15 ppm. IR:  $\tilde{\nu}$  = 3435, 1583, 1491, 1297, 1314, 1285, 1108, 843, 750, 604  $cm^{-1}$ .

Repeating with a large excess of  $N_2O_3$  (>2 equiv.) followed by column chromatography on a silica with hexane/ethyl acetate as eluent, (4,4'-dinitrophenyl)phenylamine<sup>[20]</sup>  $[(O_2NC_6H_4)_2(Ph)N]$  is isolable as yellow crystals in 90 % yield.  $^1H$  NMR:  $\delta$  = 8.15 (d, 4 H), 7.15 (d, 2 H), 7.44 (t, 1 H), 7.32 (t), 7.18 (d) ppm. IR:  $\tilde{\nu}$  = 1579, 1491, 1342, 1314, 1281, 1181 (w), 1108, 847, 750, 698  $cm^{-1}$ .

**Triethylamine:** Dry triethylamine, storing over  $CaCl_2$ , followed by distillation and storage over molecular sieves, is added dropwise to  $\approx$  10 mL of  $N_2O_3$  solution in toluene, in a 1:2 triethylamine/ $N_2O_3$  ratio. This results in rapid formation of a red color followed by darkening to brown, with a steady evolution of nitric oxide gas (1 mL yields 130 mL NO gas); a precipitate forms after a few seconds of stirring. The supernatant is decanted off within 5 min, and the precipitate is washed with cold ether under inert gas, then dried under vacuum. The composition of this precipitate has mixed anions, but corresponds to a  $\approx$  50 % conversion to an 2:1 mixture of triethylammonium nitrite/nitrate<sup>[21]</sup> as a light yellow to red semi-crystalline material.  $^1H$  NMR:  $\delta$  = 10.79 (broad s, not always seen), 3.148 (q), 1.329 (t) ppm. IR:  $\tilde{\nu}$  = 2960 (w) 2944 (m), 2738 (m), 2678 (st), 2493 (w), 1475 (w), 1386 (vs), 1265 (w) 1169 (w), 1036 (w), 847 (w), 823 (w), 802 (w)  $cm^{-1}$ . EA %: Calculated for triethylammonium nitrate ( $C_6H_{16}N_2O_3$ ): C 43.87, N 17.06, H 9.83 %. Calculated for triethylammonium nitrite.  $C_6H_{16}N_2O_2$  (148.20): calcd. C 48.61, N 18.90, H 10.90; found C 45.32, N 17.56, H 10.22, (thus ca. 67 % nitrate salt and 33 % nitrite).

With a 1:1 ratio of triethylamine to  $N_2O_3$ , and under these conditions a white or off-white product of **triethylammonium nitrite** is isolated by filtration in 48 % yield.  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  = 10.79 (broad s, not always seen), 3.148 (q), 1.329 (t) ppm. IR:  $\tilde{\nu}$  = 2980 (w), 2674 (w), 2493 (w), 1349 (m), 1192 (vs), 1168 (vs), 1072 (m) 1040 (s), 850 (m), 802 (m), 556 (w), 456 (w)  $cm^{-1}$ . UV/Vis: 370 nm. NOTE: Pure triethylammonium nitrite is aggressively deliquescent, and will dissolve in normal atmospheric conditions in minutes; in warm, humid summer air,<sup>[21]</sup> it will dissolve in a few seconds. It must be handled under inert atmosphere and carefully dried. It can be purified by sublimation. Greater quantities of water in the starting materials cause corresponding losses in yield due to dissolution. Analysis of the crude soluble reaction mixture shows minor yields of diethylnitrosamine with  $^1H$  NMR methylene peaks<sup>[22]</sup> at 4.15 (q), and 3.6 (q) as well as three other trace products of similar nature with  $\alpha$ -methylene resonances in the 3.5–4.2 ppm range in the  $^1H$  NMR spectrum.

Reversing the order of addition, that is adding the  $N_2O_3$  solution to the triethylamine solution, such that triethylamine is in excess at all times, produces the same product in similar yields, but with no gas evolution. Triturating the product with alcoholic KOH after isolation produces 1 equiv. of  $KNO_2$  per amine (the white precipitate is dried, then dissolved and triturated with HCl to determine the mass of residual KOH). As detailed in the discussion a second solution is isolated from air and purged for 5 min with argon, then triturated in situ; this allows 1.4  $KNO_2$  to be recovered per reacted amine.

**Triphenylphosphine:** One gram of triphenylphosphine is dissolved in 5 mL toluene and added to an equimolar  $N_2O_3$ /toluene solution at 0 °C, causing the evolution of nitric oxide gas and the formation of a clear solution. Evaporation yields triphenylphosphine oxide ( $O=PPh_3$ ) in 95 % yield, as a snow white powder. IR:  $\tilde{\nu}$  = 3057, 1589, 1482, 1436 (s), 1311, 1188 (s), 1121 (s), 720 (s), 696 (s), 538 (s)  $cm^{-1}$ .

When this reaction is repeated with  $N_2O_3$  in excess, and in rigorously dry conditions, the result is precipitate of a triphenylphosphine adduct. However, the presence of small amounts of moisture will cause the formation of a second product as a waxy yellow, slowly crystallizing solid, an adduct of nitric acid and triphenylphosphine oxide, Tranter's salt,<sup>[14,23,24]</sup>  $[Ph_3P=O][HONO_2]$ . IR:  $\tilde{\nu}$  = 3084, 3060, 1635 (br), 1438, 1422, 1285, 1249, 1120 (s), 1051, 947, 725, 693, 536  $cm^{-1}$ .  $^{31}P$  NMR:  $\delta$  = 34.18 ppm. Mp. 79–80 °C.

**X-ray Crystallography for  $[Bz_3NH][NO_3]$ :** A crystal mounted on a glass fiber with epoxy was subjected to single-crystal X-ray diffrac-

tion on a Bruker APEX-II CCD diffractometer equipped with a graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). SAINT<sup>[25]</sup> is used for integration of the intensity reflections and scaling and SADABS<sup>[26]</sup> for absorption correction. The structure, Figure 8, was solved by intrinsic phasing methods and subject to full least-squares anisotropic refinement for all non-hydrogen atoms. The location of non-hydrogen atoms are carried out using Fourier difference maps with the refinements solved by full-matrix least-squares method on  $F^2$  of all data using SHELXTL<sup>[25]</sup> software. Two independent molecules are present in the asymmetric unit, one of which has two disordered phenyl rings. In addition one nitrate in the asymmetric unit is disordered over two positions. Tests for merohedral twinning and attempts to solve as a tetragonal lattice failed. The hydrogen atoms positions are placed in calculated positions for all of the ordered benzyl groups but not for the aromatic groups suffering from disorder. A final ORTEP for this salt is shown in Figure 8 with additional diagrams and crystallographic data and data collection parameters are given in the Supplementary Data. The structure has been submitted to the CCDC: CCDC-1855816 for **[Bz<sub>3</sub>NH][NO<sub>3</sub>]**.

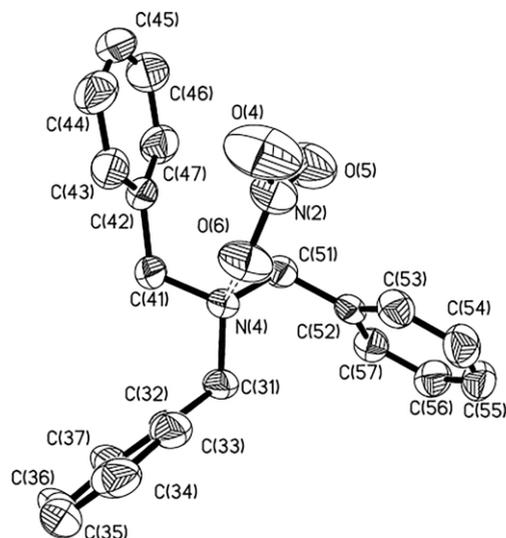


Figure 8. ORTEP image of one of the two independent molecules in the asymmetric unit of tribenzylammonium nitrate. For both independent molecules, see Figure S1.

CCDC 1855816 (for **[Bz<sub>3</sub>NH][NO<sub>3</sub>]**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**Theoretical Methods:** All of the calculations described above were performed using Gaussian 98.<sup>[27]</sup> Computations were carried out at the restricted Hartree–Fock (RHF),<sup>[28]</sup> and Density Functional Theory (DFT) levels. DFT calculations used the hybrid B3LYP functional and correlation consistent triple zeta aug-cc-pvtz basis sets.<sup>[29,30]</sup> The calculated molecular geometries were fully optimized and correspond to minima on the potential energy surface as confirmed by the absence of imaginary vibrational frequencies. Excited state energies and oscillator strengths were calculated using time dependent density functional theory.

**Supporting Information** (see footnote on the first page of this article): Details for the theoretical and crystallographic results are collected in 14 Table and 10 figures.

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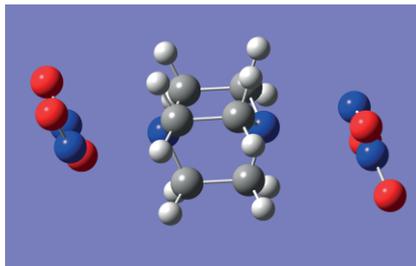
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**Chemistry of Nitrogen Oxides**

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**Isolable Adducts of Tertiary Amines  
and Dinitrogen Trioxide**



Anhydrous dinitrogen trioxide rapidly adds to tertiary amines such as DABCO to give orange solid adducts. Shown here is a DFT predicted bis adduct geometry.

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