Speciation of the Products of and Establishing the Role of Water in the Reaction of TNT with Hydroxide and Amines: Structure, Kinetics, and Computational Results

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Supporting Information



ABSTRACT: The reaction of trinitrotoluene (TNT) with bases has been investigated by NMR and visible spectroscopy methods. Hydroxide ion was found to react in one of two ways, either by deprotonation of the methyl group or by nucleophilic attack on the aromatic ring to form a σ adduct. The rate of each mode of reaction depends upon the polarity of the solvent. In tetrahydrofuran (THF), σ adduct formation is rapid and the long-term equilibrium product is deprotonation of the methyl group. When the solvent is methanol (MeOH), the two reactions have similar rates and the σ adduct becomes the majority product. Amines were found to be ineffective in directly deprotonating TNT or in forming σ adducts. Rather, the amines react with ambient water to generate hydroxide ion, which then reacts with TNT. The solvent choice and water content are crucial to understanding the reactivity of bases with TNT. To assist in the interpretation of the experimental results, computational analysis was performed at the B3LYP/6-311+G**//HF/6-311+G** level to determine the thermodynamics of the reactions of TNT. The SM8 implicit solvation model was applied to converged geometries and suggested a strong solvation effect upon product formation. Thermodynamic analysis suggested a significant preference of alkoxide or hydroxide attack versus amine attack in any modeled dielectric, consistent with the experimental observations.

INTRODUCTION

The detection of trinitrotoluene (TNT) has become an increasingly prevalent research topic over the past decade, in part because of the rise in international terrorism and the toxic nature of TNT in the environment. Many methods of detection have been proposed in the literature, including methods that rely on the reactivity of TNT arising from the electron-deficient aromatic ring. Since these reactions generate species that absorb in the visible range, simple colorimetric sensors have been developed in the solution phase.¹⁻⁴ More complex and sensitive fluorometric sensors have been developed,⁵⁻⁸ with many using the colorful species in a resonance energy transfer (RET) sensing mechanism.⁹⁻¹² In such a sensor, a donor fluorophore is chosen on the basis of significant overlap of its emission spectrum with the absorbance spectrum of the TNT product acceptor. In this fashion, a sensor can be tailored for a species that absorbs in a specific range.

Alkoxide reactions with TNT have been studied for a number of years, with two major competing reactions resulting. Scheme 1 shows the possible reactions between TNT and a generic base. Reports in the literature show that the ability of hydroxide or alkoxide to deprotonate the methyl group of

TNT, forming TNT⁻, or to attack the ring, forming the σ adduct TNT-OR^{-.13-19} While alkoxides are believed to attack the C₃ carbon of TNT, hydroxide is much less sterically hindered and is able to form the TNT-OH⁻ C₁ adduct, pushing the methyl group on TNT out of plane.³ Since C₁ was established as the most favorable site for nucleophilic attack by hydroxide ion, this is commonly attributed as the site of attack by weaker nucleophiles, such as amines.^{3,4,9-12,20-29} In the context of a rapid TNT sensor, the possible initial elementary steps are the most crucial ones to understand. Because of this, subsequent reactions such as the "Janovsky complex"¹⁴ (TNT⁻ attacking TNT) will not be discussed in this study.

In view of the multitude of TNT sensor proposals in the literature that depend on the interaction or reaction of TNT with amines, it is perhaps surprising that a thorough mechanistic study has not been undertaken previously. These types of sensors have been developed for both solution-phase and vapor-phase detection of TNT. Amine reactivity has been

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Scheme 1. Proposed Reactions of TNT with Bases^a



^{*a*}TNT can be deprotonated at its methyl group to form TNT⁻ as either free ions or an ion pair, can be attacked by a nucleophile at the C_1 or C_3 carbon to form a TNT-B σ adduct, or can have electron density donated to its electron-deficient ring to form a CT complex, TNT:B.

proposed to work in a fashion similar to that for anionic bases, where deprotonation to give TNT^{-,20–23} the formation of a zwitterionic σ complex (TNT–NR₃),^{3,9–12,24–27} and charge transfer (CT) complexes^{4,28,29} are all possible, as shown in Scheme 1. A typical approach found in the literature is to examine the absorption spectrum of TNT in solution with an amine reactant before incorporating that reactant into a solidphase sensor to project the reactivity of TNT vapor. The time domains of these studies are poorly documented. Fant et al.³ are commonly referenced for the rapid reaction of TNT with amino acids and other amines, but their reactions were performed over a 24 h period. The reactions are commonly done in solvents that may have competing reactions with TNT as well as solvents from which trace water is not easily removed. Therefore, it is possible that in this early stage of development, the reactivity may not be coming directly from the amines but rather from alternative sources such as OH⁻ generated through acid/base equilibria. For example, we have recently shown that residual water in dimethylformamide (DMF) can react with TNT to form products observable by both absorption and emission spectra.³⁰ Additionally, the observed absorption spectra are commonly misattributed to the incorrect major absorbing species. There is definite confusion as to the actual product(s) being formed in solution, as numerous accounts of the same or similar reactions lead to different proposed products; for example, the same absorption spectrum has been

explained by a CT complex, 28 TNT $^{-,21}$ or a σ adduct with an amine. 27

A recent paper by Olson et al.³¹ reported the reactions of amine bases with 2,4-dinitrotoluene. With dimethyl sulfoxide (DMSO) as the solvent, it was shown that the extent of reaction with amine bases was small. Further, at equilibrium the small amount of product formed was best attributed to deprotonation of the methyl group, not σ adduct formation. Since TNT has an additional nitro group, which makes the aromatic ring more electron-deficient, we decided to investigate whether TNT has similar reactivity to 2,4-dinitrotoluene. We used ¹H NMR spectroscopy to determine the products of the reaction of bases with TNT in tetrahydrofuran (THF) and methanol (MeOH). In nearly all cases, the amines did not react with TNT unless there was sufficient water in the system to generate hydroxide ion. Then we examined the kinetics of the reactions in these solvents using visible spectroscopy, which is more sensitive than NMR methods. We found that the rate constants depend upon the solvent system, which leads to different product distributions in different solvents.

To assist in interpreting the experimental results, computational methods were also employed here. Previous studies have restricted their structural optimization computations to molecular mechanics force fields,³² semiempirical methods,³³ and DFT methods.^{34,35} No computational studies comparing alkoxide, hydroxide, and amine reactivity through TNT⁻ formation, σ adduct formation, and CT complex formation using the same high level ab initio method have been performed, nor has solvation modeling been addressed previously. By computationally modeling the reactants and products of these proposed reactions, we were able to calculate the relative thermodynamics of each reaction and observe a significant trend in solvation.

MATERIALS AND METHODS

TNT was obtained from Drs. Jimmie Oxley and James Smith and was used without further purification. The solvents used in this study, HPLC-grade THF (99.9%, inhibitor free) and MeOH (99.9%), were purchased from Sigma-Aldrich and used as received. ACS-reagent-grade 0.1 M aqueous NaOH was purchased from Anachemia. Ethylamine (EA) (70% in water), EA in THF (2.0 M), *n*-propylamine (PA), *n*-butylamine (BA), diethylamine (DEA), and triethylamine (TEA) were purchased from Sigma-Aldrich.

NMR experiments were conducted in either THF- d_8 (99.5% D) or in CD₃OD (99.8% D), both purchased from Cambridge Isotope Laboratories. D₂O (99.8% D), DCl/D₂O (35% w/w, 99% D) solution, and NaOD/D₂O (40% w/w, 99.5% D) solution were purchased from Sigma-Aldrich. TNT solutions were quantitatively prepared, and ¹H and ¹³C spectra were acquired before and after the addition of base on a Bruker 300 MHz NMR spectrometer. The time delay from the start of the reaction to data acquisition was approximately 5 min per spectrum because of solvent locking and shimming.

Solutions containing TNT for absorbance measurements were made quantitatively using either THF or MeOH. TNT stock solution was added to a cuvette and observed prior to addition of base. While the solution was stirred, a measured amount of water and stock base solution was quantitatively added using a micropipet. Spectra were acquired with an Ocean Optics spectrometer using a white-light tungsten lamp source with the sample placed in a Peltier temperature-controlled cuvette holder held at 20.00 °C. The spectral resolution was 1 nm, and the temporal resolution was 50 ms. Experiments were prepared so that one reactant concentration would be in $100 \times$ molar excess of the other. Data were fit to exponential trends using graphing software (Microsoft Excel, SigmaPlot).

Computational modeling was performed using Spartan '10 software.³⁶ Reactants and products of TNT reactions with OH⁻, CH₃O⁻, NH₃, EA, DEA, and TEA were modeled; the generic set of reactions of TNT with base (B) can be found in Scheme 1. The amines were chosen to cover a range of basicity and steric bulk. EA is a good nucleophile and is an appropriate surrogate for the primary amines that are commonly used in the aforementioned sensors. DEA is more basic than EA but has greater steric hindrance. TEA is the best electron donor of the modeled amines but is so sterically bulky that it cannot attack the TNT ring. The deprotonation reaction was modeled using TNT⁻ with a subsequent conjugate acid as free molecules/ions or as an ion pair. σ complexes formed through nucleophilic attack at either the C1 or the C3 carbon of TNT were modeled (TNT-OH⁻ C₁, TNT-OH⁻ C₃, TNT-NH₃ C₁, etc.; see the numbering convention for TNT in Scheme 1). All species were geometrically optimized using the Hartree-Fock (HF) method with the 6-311+G** basis set and no imaginary frequencies. This gave a structure for TNT that matched the crystal structure³⁷ and reasonable geometries for the other species. Since the calculated structures were reasonable, a single-point energy calculation with the B3LYP functional and the 6-31G* basis set was used to determine the enthalpy and entropy for each species using the frequency calculation. All of the thermodynamic computations were performed using an input temperature of 298.15 K and a pressure of 1 atm. In addition, the SM8 solvation model³⁸ was applied to determine relative energies in a wide range of dielectrics in order to assist in our description of the observed solvation dependence. In these solvation computations, the converged structures from the HF outputs were used to perform single-point energy calculations at the B3LYP/6-31G* level; this approach was chosen since it was used as a fitting method for the development of the SM8 model.³⁸ To cover a wide range of dielectric constants (ϵ), the following solvent models were used: vacuum ($\epsilon = 1$), hexane (ϵ = 2.02), tetrahydrofuran (ϵ = 7.52), 1-propanol (ϵ = 20.1), methanol ($\epsilon = 33$), formic acid ($\epsilon = 58$), water ($\epsilon = 80$), and formamide ($\epsilon = 109$). ¹H NMR chemical shift estimations were also computed for each species at the same level of theory. Molecular orbital energies were obtained using the HF/6-311+G**-derived structure, the B3LYP functional, and the 6-311+G** basis set. Time-dependent density functional theory (TDDFT) calculations at this level of theory were used to determine the maxima and intensities of the six lowest-energy electronic transitions. Spectra were calculated using Gaussian line shapes with the full width at half-maximum arbitrarily set at 20 nm.

RESULTS AND DISCUSSION

Qualitative experiments were run by adding a few crystals of TNT to solutions of the various bases in THF or MeOH. In the cases of NaOH or aliphatic amines (EA, PA, BA, DEA, or TEA), there was an immediate color change indicative of chemical reaction. In contrast, the aromatic amines 2,6-lutidine, collidine, and pyridine and the weak primary amine aniline showed no color change. Further, dropping a few crystals of TNT into a few milliliters of dry TEA in the absence of cosolvent generated no visible absorbance features. Addition of a drop of water to the solution caused an immediate color change. This led us to hypothesize that the solvent played a key role in the reactivity of TNT: the hydroxide (from adventitious water in the solvents) generated by reaction with the amine was the active species in the reaction with TNT, and the amine did not react directly.

In general, a base could react with TNT by deprotonation of the methyl group, addition to the aromatic ring to form a σ adduct, or formation of a CT complex. In the case of TEA, a σ adduct with TNT is unlikely because of the steric bulk of the three ethyl groups. For the other amines, the nucleophilicity of the amine should determine the extent of the reactivity. Direct deprotonation of the methyl group on TNT should depend upon the basicity. Finally, CT complex formation should parallel the donor number (DN). For example, TEA has one of the highest DN values,³⁹ so it might be expected to donate electron density to the electron-poor TNT aromatic ring and form a CT complex. Trinitrobenzene (TNB) has been shown to form CT complexes with aliphatic amines (including TEA) in cyclohexane, with absorbance maxima in the UV range.⁴ Finally, each of the amine bases can react with water or methanol to form hydroxide or methoxide, respectively, further complicating the reactivity in these systems.

A variety of possible structures for the proposed reaction products were investigated computationally. Converged structures for the acid/base and σ complex formation reactions are shown in Figure 1 for hydroxide and methoxide and Figure



Figure 1. Converged equilibrium geometries of TNT and products from acid/base or nucleophilic addition reactions with hydroxide or methoxide. Hydroxide or methoxide are proposed to be capable of deprotonating the methyl group on TNT to form TNT⁻ or adding to either ring carbon C_1 or C_3 to form the σ adduct TNT-OR⁻.

2 for amines. The energies of all of the converged structures can be found in Table S1 in the Supporting Information. For the ion pairs, the positive hydrogen atoms on the alkylammonium cation interact directly with the oxygen atoms from the nitro group, where the greatest electron density from the TNT anion is located. This distorts the methylene group much further out of the plane of the ring than calculated for the isolated TNT anion. We were able to converge σ adducts for all of the amines with the exception of TEA. These optimizations pushed TEA away from the ring and stabilized in an electrostatic interaction or CT complex type of orientation.



Figure 2. Converged equilibrium geometries of products proposed for the reactions of TNT with amines. All of the bases gave a converged σ adduct structure except for TEA, which is expected to be too sterically hindered to attack the ring covalently.

Selected structural parameters from each species' optimized geometry are given in Table S2 in the Supporting Information. While deprotonation of the TNT methyl group depends on the base strength, formation of the σ adduct depends on the nucleophilicity. The nucleophiles show a general trend of increasing bond length as their nucleophilic strength decreases and their steric bulk increases. The largest bond angle distortions from that of TNT are seen for the TNT-OHand TNT-OCH₃⁻ adducts, stretching the ring in-plane. These adducts also distort the dihedral angles to the greatest degree of all of the nucleophiles, bending the ring out-of-plane. The amine adducts show a definite trend of increasing steric bulk resulting in increased distortion. The C1 adducts appear to distort the ring less than their C3 counterparts. In addition, the C1 adducts push the electron-donating methyl group out of the plane of the ring. Although the C₃ adducts do not displace an electron-donating group, their nucleophiles are significantly more orthogonal to the ring. This may be another stabilizing advantage of the C_1 adduct over the C_3 adduct.

 TNT^{-} formation distorts the bond angles and dihedral angles the least, which is expected because of the enhanced resonance stabilization of the ring. The most obvious change is the contraction of the C_1-C_7 bond length, indicative of vinyl character. Resonance in TNT^{-} is also supported by the smaller distortions of the O–N–O bond angles throughout the structure in comparison with the other anionic products that

have more localized charge and thus larger distortions. This is due to the lack of a nucleophile that pushes C_7 out of the plane of the ring, so the original ring planarity is largely retained. The inclusion of a counterion in the alkylammonium ion pairs leads to minimal changes in the bond lengths throughout the ring structure. The ion pairing does force a slightly increased ring bond angle distortion compared with isolated TNT⁻ and causes the ring planarity to be decreased, as observed through the increased $C_1-C_2-C_3-C_4$ dihedral angles. This deviation from planarity is reduced as the size of the counterion increases the planarity of the ring while further distorting the $C_7-C_1-C_2-C_3$ dihedral angle. The largest of these distortions comes from the pairing of TNT⁻ with the triethylammonium cation, which is attributed to the larger steric bulk. However, the distortions of these parameters for all of the investigated ion pairs are smaller than the extent of the distortions that arise from the respective nucleophilic addition.

To identify which of the predicted structures could be obtained experimentally, NMR spectroscopy was used to identify the products of reactions of the bases with TNT. The solvents used, MeOH and THF, afforded polar and slightly polar surroundings, respectively. In addition to the aliphatic amine bases, which vary in basicity, nucleophilicity, and steric bulk, NaOH was also used as a stronger base than the amines.

Reactions of TNT and sodium deuteroxide in deuterium oxide solution (NaOD/D₂O) were carried out in deuterated THF and deuterated methanol. Figure 3 shows the ¹H NMR spectra as a function of base-to-TNT ratio in THF- d_{8} , while Figure 4 shows the results of the same experiment in CD₃OD.

Figure 3 shows that the intensities of the aromatic and methyl proton peaks of TNT decrease as a function of NaOD



Figure 3. ¹H NMR spectra for the reaction of 1.3×10^{-2} M TNT with increasing concentrations of NaOD/D₂O in THF- d_8 : (a) NaOD:TNT = 0; (b) NaOD:TNT = 0.14; (c) NaOD:TNT = 0.29; (d) NaOD:TNT = 0.58; (e) NaOD:TNT = 0.94; (f) NaOD:TNT = 1.30; (g) NaOD:TNT = 1.37; (h) after addition of one drop of 30% DCl/D₂O to the solution in (g).

addition in THF- d_8 , as expected. TNT has two equivalent aromatic protons represented by the singlet at 8.98 ppm as well as three equivalent methyl protons appearing as a singlet at 2.62 ppm. Both peaks disappear with addition of NaOD as a product grows in. The growing singlet peaks (8.31 and 5.63 ppm) are observed to have a 1:1 integration ratio; this is consistent with

the formation of TNT⁻ and inconsistent with the formation of TNT-OH⁻ or a CT complex. The formation of an OD⁻ σ adduct at the C1 position should give two peaks integrating as 3:2 while a σ adduct formed at the C3 position should lead to three peaks integrating as 3:1:1. A CT complex would also give two peaks integrating as 3:2 with chemical shifts close to the spectral positions of unreacted TNT. The two ring protons at C₃ and C₅ of TNT⁻ give rise to the singlet at 8.31 ppm, while the two equivalent vinyl-type protons on C_1 appear as a singlet at 5.63 ppm. With no other features apparent in this spectrum, TNT⁻ appears to be the exclusive product on the time scale of 1 h. The relative peak positions are consistent with the report of TNT⁻ formation in DMSO/MeOH using alkoxide bases by Fyfe et al.¹³ The small shifts observed in the methyl peaks of unreacted TNT are caused by H/D exchange.⁴¹ To confirm the assignment of TNT⁻ as the product, excess DCl was added to the system. This deuterated the methylene group on TNT⁻ to form a CH₂D group (seen as a multiplet near 2.57 ppm), restored the aromatic peak at 8.98 ppm, and led to complete loss of the product peaks at 5.63 and 8.31 ppm. The ¹³C NMR spectrum of unreacted TNT in THF- d_8 (Figure S1 in the Supporting Information) displays the expected aromatic peaks at 123.1, 134.3, 146.9, and 152.4 ppm and the methyl peak at 15.4 ppm. The DEPT-135 spectrum (1 h acquisition time) recorded after the deprotonation with OD⁻ and subsequent deuteration with DCl shows the aromatic carbons containing H atoms, C_3 and C_5 , remaining at the same chemical shift (122.9) ppm) while the methyl carbon peak is no longer visible (Figure S2 in the Supporting Information). This confirms the extensive H/D exchange in the system.

In contrast, TNT⁻ is not the only product in CD₃OD (Figure 4). At a low NaOD:TNT ratio (0.24), only TNT⁻ is observed, as evidenced by the growth of singlets at 8.30 and 5.68 ppm for the C_3/C_5 protons and the CH_2^- protons, respectively. As the amount of NaOD increases, a second product grows in with peaks at 5.30 and 8.41 ppm integrating



Figure 4. ¹H NMR spectra for the reaction of 1.5×10^{-2} M TNT with increasing concentration of NaOD/D₂O in CD₃OD: (a) NaOD:TNT = 0; (b) NaOD:TNT = 0.24; (c) NaOD:TNT = 0.49; (d) NaOD:TNT = 0.97; (e) NaOD:TNT = 1.95; (f) NaOD:TNT = 2.44; (g) after addition of one drop of 30% DCl/D₂O to the sample in (f). The asterisk indicates an impurity in the sample.

to a 3:2 ratio, which is consistent with the C_1 deuteroxide σ adduct formation, where the lower-field feature represents the two ring protons (on C_3 and C_5) and the higher-field feature represents the methyl group protons. Deuterium exchange can be observed with the methylene group on TNT⁻, as the peak at 5.68 ppm diminishes and subsequently disappears while the ring protons on TNT⁻ remain visible, ultimately leading to deuteration to give CHD⁻ and CD₂⁻ groups. Finally, at higher NaOD:TNT ratios, another feature becomes apparent at 8.82 ppm that is unassigned. This resonance may arise from the aromatic protons on a deuterated TNT molecule or may be from a further decomposition product. Addition of DCl to the last point in the titration did not completely restore TNT, which is different than the behavior observed in THF. TNT was exposed to DCl as a control for this experiment, and no change to the original TNT features was observed.

Our results differ from Fyfe's observation of a 1:1 ratio for the C_3 adduct of methoxide,¹³ where two singlets were detected at 8.45 and 6.18 ppm in 87.5% DMSO/12.5% MeOH. It is also important to note that the products make up only a small percentage of the total integration at equimolar TNT and NaOD concentration; this suggests that the equilibria lie much further toward reactants in MeOH than in THF.

The ¹³C NMR spectrum of unreacted TNT in CD_3OD (Figure S3 in the Supporting Information) is similar to that observed in THF- d_8 . After the addition of DCl to the NaOD/TNT system, a ¹³C DEPT 135 experiment was undertaken. The data (Figure S4 in the Supporting Information) also support the deuteration of the TNT⁻ methylene to create a mixture of CH₂D, CHD₂, and CD₃ groups. The CHD₂ group appears as a positive feature at 15.5 ppm, while the CH₂D group is a negative feature centered at 15.1 ppm and split into three peaks (14.8 and 15.3 ppm) by the D atom.

Figure 5 shows the ¹H NMR spectra of TNT mixed with various alkylamines in THF- d_8 . The different amines show four modes of reactivity: TEA shows no reaction; DEA and BA



Figure 5. ¹H NMR spectra for the reaction of TNT upon addition of bases in THF- d_8 : (a) unreacted TNT (1.5×10^{-2} M); (b) TNT (1.4×10^{-2} M) + NaOD (8.1×10^{-3} M); (c) TNT (2.7×10^{-1} M) + DEA (1.3 M); (d) TNT (2.7×10^{-1} M) + TEA (0.91 M); (e) TNT (2.7×10^{-1} M) + EA/H₂O (0.92 M); (f) TNT (2.7×10^{-1} M) + PA (1.4 M); (g) TNT (2.7×10^{-1} M) + BA (0.73). Peaks for the unreacted amines are found upfield from 5 ppm with significantly higher intensities than in the spectra shown.

show a single product that is not TNT⁻; PA gives peaks consistent with the formation of TNT⁻, albeit exchangebroadened; and EA displays peaks for TNT⁻ and a second product. The observations of TNT⁻ do not correlate well with the expected basicities of the amines in water; however, they do correlate well to the water content. EA is an aqueous solution and the PA used was wet. In the cases of DEA, TEA, and BA, which were dry, no TNT⁻ was observed, but the addition of water to the sample generated spectra similar to those seen for EA and PA. This suggests that none of the alkylamines are strong enough bases to directly deprotonate the methyl group on TNT.

The products of the reactions of BA and DEA with TNT and the second product of the reaction with EA are assigned to Nbased σ adducts. BA shows a single feature at 7.60 ppm that is a broadened triplet, indicating that the resonance originates from a CH₂ group on the BA. There is not enough spectral information to indicate if the BA adds to the C_1 or C_3 position. The second product from EA has peaks at 7.23 and 5.91 ppm that have no splitting, suggesting that either the product is a hydroxide σ adduct or that the exchange is too severe to resolve any coupling. The spectrum resulting from the reaction of DEA is well-resolved with quartets at 7.22 and 6.55 ppm and singlets at 5.48, 5.53, and 7.94 ppm, suggesting formation of σ adducts rather than TNT⁻. The observation of two quartets, arising from the CH₂ groups on DEA, and two singlets, originating from the methyl group on TNT, suggests that two σ adducts form. DEA is expected to be more nucleophilic than the primary amines but not bulky enough to prevent reaction at either C_1 or C_3 . However, the observation of only one peak in the 8 ppm region implies that the DEA attacks only a single site. The observed spectrum for the DEA is assigned as two conformers of a C₁ addition. The location of the ethyl groups on the nitrogen atom leads to the two structures: in the lowerenergy case the ethyl groups are located adjacent to the nitro groups, while in the second case there is rotation by $\sim 90^{\circ}$ so that one ethyl group is adjacent to the ring and the other is adjacent to the methyl group. These structures are shown in Scheme 2. The calculated energy difference (in vacuum, DFT/ B3LYP/HF6-311G*) is ~35 kJ/mol.

Figure 6 shows the vinyl region of the ¹H NMR spectra for the reactions of TNT with the amine bases in CD_3OD . The same major features appear here for the TNT⁻ anion at 8.3 and 5.6 ppm, with the "wet" amines showing higher amounts. As seen in the NaOD titration in MeOD, there is obvious H/D







Figure 6. ¹H NMR spectra for the reaction of TNT with added bases in CD₃OD: (a) unreacted TNT (2.9×10^{-1} M); (b) TNT + NaOD; (c) TNT (2.9×10^{-1} M) + DEA (8.7×10^{-2} M); (d) TNT (2.9×10^{-1} M) + TEA (8.7×10^{-2} M); (e) TNT (2.9×10^{-1} M) + EA/H₂O (8.7×10^{-2} M); (f) TNT (2.9×10^{-1} M) + PA (8.7×10^{-2} M); (g) TNT (2.9×10^{-1} M) + BA (8.7×10^{-2} M). Peaks for the unreacted amines are found upfield from 5 ppm with significantly higher intensities than in the spectra shown.

exchange of the methylene hydrogens that leads to the loss of the signal at 5.6 ppm relative to the aromatic protons at 8.3 ppm. The addition of the amines to MeOD may also generate methoxide (which is also capable of deprotonating TNT) through an acid/base equilibrium. Since the TNT⁻ features are barely above the level of noise, it is also possible that other products may be formed in amounts below the detection limits. The unreacted TNT signals (not shown) are the predominant features, with intensities approximately 500 times those of the products. Clearly, the equilibria for these reactions lie much closer to reactants than products.

NMR chemical shifts were calculated for reactions of TNT with hydroxide ion, to compare to the experimentally available data. Table 1 shows the comparison of the computations (in vacuum) to the experimentally observed features in tetrahydrofuran (THF) and methanol (MeOH). Although the values differ based on the lack of solvation in the calculations, the differences are in a reasonable range to account for solvent shifts. There are only small chemical shifts effects when

Table 1. Comparison of Computed and Experimental ¹H NMR Data for TNT and Alkoxide Reactions^{*a*}

		computed	observed	
species	protons	(vacuum)	THF	MeOH
TNT	aromatic H	8.320	8.97	8.96
	methyl H	2.107	2.62	2.64
TNT ⁻	aromatic H	7.752, 7.733	8.30	8.29
	methyl H	4.854, 4.829	5.64	5.68
$TNT-OH^-C_1$	aromatic H	7.597, 7.482	N.O.	8.41
	methyl H	1.461	N.O.	5.28
$TNT-OH^-C_3$	aromatic H	7.938, 5.895	N.O.	N.O.
	methyl H	1.630	N.O.	N.O.

^aN.O. indicates that the product was not observed. All of the predicted and observed peaks were singlets. The computed value for each methyl group is the average of the three computed chemical shifts.



changing from the nonpolar THF to the more polar methanol system. The calculated chemical shifts, in comparison, are found at lower field than their experimental counterparts, as expected, especially given the relatively small basis set used. The magnitude of the solvation shifts (from calculated to experimental) are all approximately the same, at about 0.5 to 0.9 ppm shifted downfield. The one significant outlier here is the computation for the methyl protons in TNT–OH⁻; while the change of the adjacent carbon from sp² to sp³ hybridization would be expected to lower the chemical shift, the inclusion of the hydroxyl group in close proximity would be expected to raise the chemical shift. With additional reorientation of the nitro groups, it is not implausible to observe a shift higher than 5 ppm, as observed in methanol.

The electronic structures of the various TNT reaction products were calculated in order to assist in understanding the visible spectra. Figure 7 shows the computed energies of the



Figure 7. Computed MO diagram for the explored TNT products with bases at the B3LYP/6-311+ $G^{**}//HF/6$ -311+ G^{**} level. Double arrows indicate the HOMO for each species.

frontier molecular orbitals of TNT and the discussed products of the alkoxide and amine reactions. TNT has its occupied MOs at the lowest energy relative to those of the other species and has the largest HOMO–LUMO gap, which is consistent with the experimental observation of no visible absorbance maxima. The anionic species TNT⁻, TNT–OH⁻ C₁, TNT– OH⁻ C₃, TNT–OCH₃⁻ C₁, and TNT–OCH₃⁻ C₃ all have very similar MO energies. TNT⁻ is shown here to have the smallest HOMO–LUMO gap, which is consistent with the spectral assignments made previously in absorbance measurements.^{13,14} Of the two hydroxide adducts, the C₁ adduct has a lower HOMO–LUMO gap and is expected to have an absorbance maximum at longer wavelength than the C₃ adduct. The energies of the HOMOs and LUMOs are given in Table S5 in the Supporting Information.

The amine adducts show a size-dependent trend of MO energies, where increased steric bulk destabilizes the MOs. This is true for both the C_1 and the C_3 adducts, but with little difference in the MO energies of each C_1/C_3 adduct pair. There is significant difference between the energies of the amine

adducts versus the alkoxide adducts. This corresponds to the structural analysis, where the amines do not distort the central ring of TNT as significantly as OH^- or CH_3O^- . Since the HOMO surfaces are localized on the aromatic ring, larger distortion raises the relative MO energies.

Figure 8 shows the TDDFT-calculated electronic spectra for TNT⁻ and the C_1 and $C_3 \sigma$ adducts for OH⁻ (Figure 8a),



Figure 8. Absorption spectra computed at the B3LYP/6-311+G**// HF/6-311+G** level, normalized to individual species' computed maxima. (a) TNT–OH⁻ C₁ (black solid line), TNT–OH⁻ C₃ (red dashed line), TNT⁻ (blue dot-dashed line); (b) TNT–OCH₃⁻ C₁ (black solid line), TNT–OCH₃⁻ C₃ (red dashed line); (c) TNT–EA C₁ (black solid line), TNT–EA C₃ (red dashed line); (d) TNT–DEA C₁ (black solid line), TNT–DEA C₃ (red dashed line).

CH₃O⁻ (Figure 8b), EA (Figure 8c), and DEA (Figure 8d). The predicted spectra for the OH⁻ and CH₃O⁻ σ adducts suggest that bonding to C1 should give two spectral peaks (Figure 8a, black solid line) while bonding to C_3 should give three peaks (Figure 8a, red dashed line). Thus, the electronic spectra may be able to distinguish the two species. In addition, TNT⁻ also shows three peaks, with the lowest-energy transition of all of the computed species (Figure 8a, blue dot-dashed line). TNT⁻ is expected to have an absorption band in the lowerenergy region of the visible range, allowing for a unique signal at which only TNT⁻ can be detected. In contrast, the amine adducts show similar doublets for either C_1 or C_3 attack. Because of this, no distinction between amine adduct species is likely to be observed in the electronic spectra. The wavelengths and intensities used to calculate the spectra in Figure 8 are given in Table S5 in the Supporting Information.

Having good evidence for the products formed by TNT and hydroxide, we conducted experiments in which we observed the visible absorption spectrum for 5 min after the reaction was started. Briefly, we are dealing with the following competing equilibria:

$$\Gamma \mathrm{NT}(\mathrm{solv}) + \mathrm{OH}^{-}(\mathrm{solv}) \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} \mathrm{TNT}^{-}(\mathrm{solv}) + \mathrm{H}_2\mathrm{O}(\mathrm{solv})$$
(1)

$$TNT(solv) + OH^{-}(solv) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} TNT - OH^{-}(solv)$$
(2)

To determine the rate constants for the concurrent formation of TNT⁻ and TNT–OH⁻, we derived an expression to fit the absorbance data as a function of time. The full derivation can be found in the Supporting Information. To obtain pseudo-firstorder conditions, one of the reactants must be in large excess over the other and the H₂O concentration must be much larger than the TNT⁻ concentration. In order to meet the latter condition, water was added to each solvent. Under these conditions, the concentration of each product can be monitored as a function of time using a single exponential rise function:

$$[\text{product}] = a(1 - e^{-k_{\text{obs}}t})$$
(3)

where the pre-exponential factor a and the observed rate constant k_{obs} are functions of intrinsic rate constants and initial concentrations of reactants. Substituting the absorbance for the concentration using Beer's law yields

$$A_{\rm prod} = \varepsilon_{\rm prod} b a (1 - e^{-\kappa_{\rm obs} t}) \tag{4}$$

where $A_{\rm prod}$ is the absorbance of the product, $\varepsilon_{\rm prod}$ is the molar absorptivity of the product at the monitored wavelength, and *b* is the path length (1 cm for all of the experiments reported here). Under pseudo-first-order conditions, the time evolution can be treated independently (see the Supporting Information), so in cases where both TNT⁻ and TNT-OH⁻ absorb at the same wavelength, eqs 4 for the two species (i.e., with different $\varepsilon_{\rm prod}$, *a*, and $k_{\rm obs}$ values) are summed to account for the total absorbance.

In Figure 9, we observe that the reaction of TNT with excess NaOH in THF forms two products, one that grows in immediately and the other that forms more slowly. However,



Figure 9. Initial 5 min absorbance experiment observing the products of 4.2×10^{-3} M NaOH reacting with 4.2×10^{-5} M TNT in THF: (a) 5.21 s; (b) 22.96 s; (c) 95.13 s; (d) 153.70 s; (e) 214.10 s; (f) 289.78 s. Note the spectral shape change early on, consistent with the OH⁻ σ adduct giving way to TNT⁻ as the major absorbing species. The inset shows fits of the absorbance data from 520 and 700 nm to eq 4.

the second product is clearly the major absorbing species even before equilibrium is established. The spectrum of the initial product has the shape of an anionic σ adduct, TNT-OH⁻, with $\lambda_{\text{max}} \approx 440$ nm, a second maximum at ~510 nm, and a largely featureless tail into longer wavelengths. The spectrum of the second product belongs to TNT⁻,^{13,14} typified by a doublet at about 500 and 525 nm and a broad maximum at 650 nm. This is consistent with the TDDFT calculations, which predicted two peaks for TNT-OH⁻ and three peaks for TNT⁻. The ¹H NMR spectra in THF showed only the presence of TNT⁻, indicating that the amount of TNT-OH⁻ found is small, below the detection limit of the NMR experiment. Figure 10 shows



Figure 10. Initial 5 min absorbance experiment observing the products of 2.2×10^{-3} M TNT reacting with 2.2×10^{-5} M NaOH in THF: (a) 0.00 s; (b) 0.38 s; (c) 0.75 s; (d) 5.33 s; (e) 14.35 s; (f) 61.57 s; (g) 108.63 s. The inset shows fits of the absorbance data from 520 and 700 nm to eq 4.

spectra from the reaction of excess TNT with NaOH in THF. A similar, but not identical, spectral shape compared to the excess NaOH experiment is seen. The relative intensity of the doublet at 500 and 525 nm is reversed, indicating TNT-OH⁻ formation early but eventually disappearing. A control experiment was conducted to determine the effect of a possible scattering component of NaOH in THF on the kinetic fits. We observed a reasonably significant baseline increase with the addition of NaOH to THF, which dissipated within a few seconds. This led us to omit some initial data when finding rate constants when the absorbance signal was on a similar order of magnitude as the scattering. Figures S5–S10 in the Supporting Information show the data for different initial concentrations of TNT.

When MeOH was used as the solvent, different results were observed, as shown in Figure 11. When hydroxide ion is in excess, TNT⁻ is the predominant absorbing species early on, as indicated by the broad features at 515 and 650 nm and the low absorbance at 440 nm. After some time, TNT-OH⁻ evolves, as evidenced by the increase in absorbance at 440 nm. This is consistent with the order of appearance of these species in the ¹H NMR spectra. Figure 12 shows the experiment with excess TNT in MeOH. These spectral features are consistent with TNT-OH⁻ formation, while there is still slight evidence to suggest a small TNT⁻ component given the small shoulder in the absorption spectrum at 650 nm. Also, it should be noted that the relative absorbances of the feature at 450 nm and the feature at 520 nm change slightly over the course of the observation; this implies that more than one species is being observed. Figures S11-S16 in the Supporting Information show the data for several concentrations of NaOH and TNT.



Figure 11. Initial 5 min absorbance experiment observing the products of 2.5×10^{-2} M NaOH reacting with 2.5×10^{-4} M TNT in MeOH: (a) 0.14 s; (b) 0.79 s; (c) 4.09 s; (d) 9.02 s; (e) 55.69 s; (f) 172.51 s; (g) 268.17 s. The inset shows fits of the first 15 s of absorbance data from 520 and 700 nm to eq 4; in this case, the data at 520 nm required two exponential rise functions for a proper fit.



Figure 12. Initial absorbance experiment observing the products of 4.1 $\times 10^{-2}$ M TNT reacting with 4.1 $\times 10^{-4}$ M NaOH in MeOH: (a) 0 s; (b) 0.50 s; (c) 4.83 s; (d) 5.10 s; (e) 5.39 s; (f) 5.67 s; (g) 6.23 s. The spectrum increases then decreases, with no additional features appearing during the observation. The inset shows fits of the first 10 s of absorbance data from 520 and 700 nm to eq 4.

Equation 4 was used to find rate constants for all of the data in both THF and MeOH. In cases where both TNT- and TNT-OH⁻ were observed, a sum of two exponentials was used with the assumption that reactions shown in eqs 1 and 2 could be treated independently. Only the early time data were used, before any decays in absorption were observed. The observed rate constants and pre-exponential factors can be found in Table 2. The observed rate constants found at the two different wavelengths are reproducible within the anticipated errors of the kinetic method. As discussed above, in THF, the major absorbing species is TNT⁻. In MeOH, the excess NaOH experiments show TNT⁻ as the major absorbing species, while the excess TNT experiments show TNT-OH⁻ as the major absorbing species. To find the intrinsic rate constants, the molar absorptivities of each absorbing species need to be found at each wavelength.

The molar absorptivity of TNT⁻ ($\varepsilon_{\text{TNT}^-}$) was calculated in THF under the assumption that all of the TNT was deprotonated in excess OH⁻ with the sole product being TNT⁻, which is appropriate on the basis of the ¹H NMR titration data. With the extrapolated absorbance at equilibrium and the initial TNT concentration, the resulting calculations yielded $\varepsilon_{\text{TNT}^-}$ = 4000 and 11 200 L mol⁻¹ cm⁻¹ at 700 and 520 nm respectively. Unfortunately, the same reaction in MeOH was shown to be more complicated by NMR spectroscopy, so the same approach was not appropriate for calculating the molar absorptivity of TNT- in MeOH. The pre-exponential factors can be used to find the molar absorption coefficient at 520 nm for TNT-OH-. Each pre-exponential factor found in the kinetic fits represents the fraction of the absorption at infinite time attributable to each species, TNT- and TNT-OH⁻. If it is assumed that the limiting reagent is completely consumed in these reactions, then $a_{\text{TNT}^-} = \varepsilon_{\text{TNT}^-} f_{\text{TNT}^-} [L]_{0}$ where f_{TNT^-} is the fraction of reaction that ends up as TNT⁻ and $[L]_0$ is the initial concentration of the limiting reagent. Likewise, $a_{\text{TNT-OH}^-} = \varepsilon_{\text{TNT-OH}^-} f_{\text{TNT-OH}^-} [L]_0$ and $f_{\text{TNT}^-} +$ $f_{\text{TNT-OH}^-} = 1$, so we find the average $\varepsilon_{\text{TNT-OH}^-}$ at 520 nm to be ~400 L mol⁻¹ cm⁻¹ in THF.

Table 2. Observed rate constants and pre-exponential factors for pseudo-first order TNT + NaOH experiments in THF and MeOH calculated by fitting absorbance data at 520 or 700 nm to eq 4. The values in parentheses are the standard errors of the fit for the last digit of the reported constant

			TNT			TNT-OH-		
			700 nm		520 nm		520 nm	
$[TNT]_0(M)$	$[OH^{-}]_{0}(M)$	$[H_2O]_0 (M)$	$k_{\rm obs}~({\rm s}^{-1})$	a (a.u.)	$k_{\rm obs}~({\rm s}^{-1})$	a (a.u.)	$k_{\rm obs}~({\rm s}^{-1})$	a (a.u.)
			Rea	actions in THF				
4.4×10^{-5}	4.4×10^{-3}	2.3	$7.6(1) \times 10^{-3}$	0.186(1)	$6.7(1) \times 10^{-3}$	0.516(3)	0.18(2)	0.064(4)
3.3×10^{-5}	3.3×10^{-3}	1.7	$7.1(2) \times 10^{-3}$	0.123(1)	$6.1(1) \times 10^{-3}$	0.343(3)	0.27(2)	0.059(3)
2.2×10^{-5}	2.2×10^{-3}	1.1	$7.8(1) \times 10^{-3}$	0.0825(5)	$7.0(1) \times 10^{-3}$	0.2310(9)		
2.2×10^{-2}	2.2×10^{-4}	0.14	$7.3(2) \times 10^{-3}$	0.123(1)	$3.9(4) \times 10^{-3}$	0.503(7)	0.026(3)	0.12(2)
1.7×10^{-2}	1.7×10^{-4}	0.11	$7.0(2) \times 10^{-3}$	0.0832(7)	$5.7(2) \times 10^{-3}$	0.312(2)	0.04(1)	0.018(4)
1.3×10^{-2}	1.3×10^{-4}	0.091	$8.0(3) \times 10^{-3}$	0.0489(6)	$5.3(5) \times 10^{-3}$	0.166(3)	0.033(8)	0.034(7)
			Read	ctions in MeOH				
3.3×10^{-4}	2.5×10^{-2}	13	0.73(2)	0.185(2)	0.9(2)	0.3(2)	0.33(8)	0.4(2)
2.2×10^{-4}	1.8×10^{-2}	9.3	0.85(2)	0.12(2)	0.83(1)	0.401(4)		
1.5×10^{-4}	1.4×10^{-2}	6.8	0.75(2)	0.060(2)	0.90(3)	0.185(3)		
4.1×10^{-2}	4.0×10^{-4}	1.1					1.22(5)	1.32(3)
2.9×10^{-2}	2.9×10^{-4}	0.7					2.1(3)	0.82(9)
2.2×10^{-2}	2.2×10^{-4}	0.6					1.7(1)	0.33(1)
1.4×10^{-2}	1.4×10^{-4}	0.4					2.8(2)	0.074(3)

The intrinsic rate constants for the reactions between TNT and OH⁻ can be estimated using the observed fits and the absorption coefficients. The forward rate constants k_1 and k_2 are found from the slopes of plots of ak_{obs} versus $[TNT]_0[OH^-]_0$, which are equal to εk_i (i = 1, 2). The reverse rate constants k_{-1} and k_{-2} are found from k_{obs} . The slope of a plot of k_{obs} versus $[H_2O]_0$ gives k_{-1} when TNT⁻ is the observed species and $k_{obs} = k_{-2}$ when TNT-OH⁻ is monitored. All of these plots are shown in Figures S17–S20 in the Supporting Information. The intrinsic rate constants for each solvent are given in Table 3,

Table 3. Intrinsic Rate Constants and Thermodynamic Parameters for the Reaction of TNT with OH^- at 20 °C^{*a*}

in THF	in MeOH
1.3(1)	$3(2) \times 10^{5*} (520 \text{ nm})$ $2.0(8) \times 10^{5*} (700 \text{ nm})$
$2.2(3) \times 10^{-4}$	$5(3) \times 10^{-3}$
2(1)	$1.1(5) \times 10^{5*} (520 \text{ nm})$
0.03(2)	1.9(6)
$6(2) \times 10^{3}$	
$7(6) \times 10^{1}$	
-22(2)	
-10(2)	
	in THF 1.3(1) 2.2(3) $\times 10^{-4}$ 2(1) 0.03(2) 6(2) $\times 10^{3}$ 7(6) $\times 10^{1}$ -22(2) -10(2)

^{*a*}Each value in parentheses is the uncertainty in the last digit of the reported constant. Values labeled with a * are εk_{ν} where the molar absorption coefficients in MeOH are unknown.

except for those cases where the absorption coefficient is not known. The reverse rate constant for the deprotonation reaction is about 10 times larger in MeOH than in THF, accounting for the more complicated speciation in MeOH. Also given in Table 3 are the equilibrium constants for eqs 1 and 2 ($K_{eq}[1]$ and $K_{eq}[2]$, respectively) and ΔG° for each reaction at 20 °C in THF. The equilibrium constants were estimated from the rate constants as $K_{eq}[1] = k_1/k_{-1}$ and $K_{eq}[2] = k_2/k_{-2}$.

The NMR experiments and qualitative tests indicated that the amine reacted with TNT only in the presence of water. Furthermore, additional products were observed in the NMR spectra for some amines, indicating additional complexity in the reaction between TNT and the amine bases. To attempt to understand the kinetics of the reaction between the amine bases and TNT, the visible spectra of the new products needed to be determined. This was done using THF as the solvent, as shown in Figure 13. As noted above, the spectrum of the equilibrium product of TNT reacting with excess NaOH is that of nearly pure TNT⁻, while when TNT is in excess both TNT⁻ and TNT–OH⁻ spectral features are observed.

On the basis of the TDDFT calculations, we made the assumption that $TNT-OH^-$ has minimal absorption at 700 nm and normalized the TNT^- spectrum to match the mixed spectrum at that wavelength. This assumption is justified by noting that the band shape of the normalized TNT^- spectrum and the mixed spectrum match identically from 680 nm to the 800 nm baseline. The difference spectrum, shown in Figure 13A3, then represents the spectrum of $TNT-OH^-$. The same process was followed for the spectra of the amine reaction products. The spectrum for TNT^- was first normalized to 700 nm, as shown in Figure 13B1-G1. Again, the band shapes from ~670 to 800 nm were identical for all of the amines, showing that this region in all of the spectra is dominated by TNT^- absorption. Figure 13B2-G2 shows the difference spectra with the TNT^- component removed. Then the $TNT-OH^-$

spectrum was normalized to match the absorbance at 563 nm in each spectrum, as shown in Figure 13B2–G2.

Again, the band shapes from 550 to 800 nm were identical, supporting the assumption that this spectral region mainly arises from absorption by TNT-OH⁻. Finally, the TNT-OH⁻ component was removed to give the spectra shown in Figure 13B3-G3. A similar process was done for the spectra taken in excess TNT, where the experimental spectra and the final difference spectra are shown in Figure 13B4-G4. In excess base, the primary amines, EA, PA, and BA have few or no spectral components for which TNT⁻ and TNT-OH⁻ do not account, with most of the absorbance attributed to TNT-. There is little difference between the spectra using EA or EA/ H₂O, indicating that there is sufficient water in "dry" THF to allow the reaction to occur. With excess TNT, all of the amines show a feature that can be assigned to a nitrogen-based σ adduct, TNT-B, and this accounts for most of the absorbance in the visible region (the large tail below 425 nm is the edge of the TNT UV absorption). For DEA, EA, PA, and BA, these features are consistent with the NMR spectra. For the case of excess TEA, there is no peak in the 400-500 nm region, and only small contributions from TNT- and TNT-OH- are observed. Consistent with the NMR spectroscopy results, the extent of reaction for the amines with TNT is small, only a few percent in each case. Estimation of the percent formation of the N-based σ adduct is not possible because the molar absorption coefficient is not known at any wavelength. However, in excess base, DEA had the largest feature assigned to TNT-DEA, consistent with the NMR spectroscopy data. Other than for the 70% aqueous solution of EA, no additional water was added to these samples. Thus, the reactivity arises from hydroxide generated by residual water from the solvents or absorbed from humidity in the air. This in part limits the extent of reaction. However, even for the aqueous EA sample, the percent conversion to the anions is low. It should be recalled that when neat amine is used as the solvent, no reaction is observed unless water is added to the system, supporting the need for water for any reaction to occur.

The N-based σ adduct is the predominant product under excess TNT conditions, which is counterintuitive. This demonstrates the role of the hydrolysis reaction of the amine. In the experiments with excess TNT there is negligible OH⁻ available to react, perhaps as much as 4 or 5 orders of magnitude less hydroxide than TNT. This allows for the amine base to attack the aromatic ring to form the N-based σ adduct. In the case of excess base, the amine reacts with water, presumably with a higher rate, to generate hydroxide ion, which then reacts with the TNT. This drives the hydroxide equilibria until all of the TNT is consumed, leaving little TNT to form TNT-B.

Figure 14 shows the same spectral analysis in MeOH. To estimate the pure TNT⁻ spectrum, a spectrum taken after 1 s of reaction was used. This is consistent with the NMR spectroscopy data (Figure 4b) showing that at modest TNT:OH⁻ ratios only the deprotonated anion was observed. The TNT-OH⁻ spectrum was estimated from the same reaction after 300 s and found by difference. Once the TNT⁻ and TNT-OH⁻ spectra in MeOH were determined, the same procedure as used for THF was followed to deconvolute the spectra for the amine bases. The conclusions about the reactivity are similar for THF and MeOH on the basis of the visible spectra.

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Figure 13. Spectra of the reaction products of various bases with TNT in THF after 300 s. Row A: (A1) 2.2×10^{-5} M TNT + 2.2×10^{-3} M OH⁻, giving exclusively TNT⁻; (A2) black line 2.2×10^{-3} M TNT + 2.2×10^{-5} OH⁻, red dashed line TNT⁻ contribution; (A3) TNT–OH⁻ spectrum found as the difference of the spectra from A2. Row B: EA. Row C: EA/H₂O. Row D: PA. Row E: BA. Row F: DEA. Row G: TEA. For the amine bases, the columns show the following spectra: Column 1: black line, product with 100× excess base; red dashed line, TNT⁻ contribution. Column 2: black line, TNT⁻ contribution removed; red dashed line, TNT–OH⁻ contribution. Column 3: black line, residual absorbance from a σ adduct or CT complex. Column 4: black line, product with 100× excess TNT; blue dashed line, residual absorbance after removal of TNT⁻ and TNT–OH⁻ contributions.

On the basis of the experimental observations, the mechanism of the reaction of TNT with the amines must include hydrolysis to generate hydroxide ion and the ammonium cation, as shown in eq 5:

$$B(solv) + H_2O(solv) \rightleftharpoons HB^+(solv) + OH^-(solv)$$
(5)

The equilibrium constant for this reaction is on the order of $10^{-5}-10^{-6}$, depending upon the base. Since no reaction is observed in neat amine bases, direct deprotonation of TNT by the amine and attack of the amine to form the σ adduct can be ruled out. Under those conditions where a σ adduct can be observed, it must occur by reaction of TNT⁻ or TNT-OH⁻ with either the amine or the ammonium cation (eqs 6–8):

$$\text{TNT}^{-}(\text{solv}) + \text{HB}^{+}(\text{solv}) \rightleftarrows \text{TNT} - B(\text{solv})$$
 (6)

$$TNT-OH (solv) + B(solv)$$

$$\Rightarrow TNT-B(solv) + OH^{-}(solv)$$
(7)

$$TNT-OH^{-}(solv) + HB^{+}(solv)$$

$$\Rightarrow TNT-B(solv) + H_{2}O(solv)$$
(8)

We have no evidence to establish which of these equilibria, if any, are dominant. Even under excess reactant conditions, the mechanism is too complicated to solve the rate equations in a simple closed form. In the case of MeOH, we did not consider



Figure 14. Spectra of the reaction products of various bases with TNT in MeOH. All of the spectra were measured after 300 s of reaction. The spectra on the left are under 100-fold excess base conditions, and the spectra on the right are under 100-fold excess TNT conditions. For each amine base, the red dotted line shows the contribution of TNT⁻ to the experimental spectrum, the green dotted line shows the contribution of TNT–OH⁻ to the experimental spectrum, and the blue dashed line is the remaining component, assigned to the N-based σ adduct. The same procedure as described in Figure 13 was used to subtract the TNT⁻ and TNT–OH⁻ components from each of the observed spectra.

the possibility that hydroxide deprotonates the alcohol and the methoxide ion contributes to the overall reactivity because the equilibrium constants are small.⁴²

As an example of the temporal evolution of the reaction, Figure 15 shows the absorbance as a function of time for the reaction of TNT with DEA under conditions of excess TNT and excess DEA in both THF and MeOH. The prominence of the TNT⁻ spectrum is evident early in the reaction for all of the spectra except that for excess TNT in THF. As the reaction proceeds, the product(s) predominantly become either TNT-OH⁻ or the nitrogen-centered σ adduct TNT-DEA. In the case of excess TNT in THF, the primary products are the σ adducts, although detailed analysis did show a small TNT⁻ component. On the basis of the NMR spectroscopy results, the



Figure 15. Absorbance evolution for the reaction of TNT with DEA in (left) THF and (right) MeOH: (top left) 8.68×10^{-3} M TNT + 0.90 M DEA in THF from t = 0 to 150 s; (bottom left) 0.352 M TNT + 3.5×10^{-3} M DEA in THF from t = 0 to 253 s; (top right) 3.44×10^{-3} M TNT + 0.34 M DEA in MeOH from t = 0 to 229 s; (bottom right) 0.101 M TNT + 1.0×10^{-3} M DEA in MeOH from t = 0 to 52 s.

primary product in THF after 5 min of reaction is the N-centered σ adduct, which is consistent with the visible spectra.

The time-dependent spectra for all of the amines were used to determine the observed rate constants for the reactions with these bases, which are reported in Table 4. The data were fit to biexponentials in most cases, with the fast process being assigned to formation of TNT⁻ and the slow process being assigned to formation of the σ adducts TNT-OH⁻ and/or TNT-B. In the case of TEA, there also may be a contribution from a CT complex.⁴⁰ The observed rate constants showed no pattern as the initial concentration of either TNT or base was changed by small amounts (factors of 2 or 3), so the reported values are averages over all measurements. The effect of the solvent is modest, but generally the reaction to form TNTproceeds 2-3 times faster in THF than in MeOH, although the reaction of DEA is 10 times faster in THF under excess TNT conditions. In excess base, the observed rate constants are similar in the two solvents for the primary amines, while DEA and TEA react more rapidly in MeOH. Formation of the σ adducts gives similar rate constants for the two solvents with either reactant in excess. The key finding, though, is that the amines require the presence of water to react under any set of conditions.

In an attempt to understand the different reactivities of TNT with bases in the two solvents, thermodynamic parameters were estimated using the DFT results. Table 5 shows the parameters $\Delta E_{rxn}^{\circ}, \Delta G_{rxn}^{\circ}, \Delta H_{rxn}^{\circ}$, and ΔS_{rxn}° calculated for acid/base and nucleophilic addition reactions between TNT and several bases in vacuum. All of the reactions, both acid/base and nucleophilic addition, with the anionic bases are calculated to be favorable, while none of these reactions are favorable for the amine bases. For the reaction of TNT with hydroxide or methoxide, ΔG° is similar for the acid/base and nucleophilic addition reactions for each anion (although all of the reactions with OH⁻ are more favorable by more than 100 kJ/mol compared with CH₃O⁻), which suggests that a mixture of products should be observed experimentally. There is a distinction in the entropy change, which is slightly favorable for the acid/base reactions but unfavorable for the nucleophilic addition reactions. This implies that the speciation in the reaction should change considerably depending upon temperature.

Table 4. Observed rate constants for the reactions of amine bases with TNT. The reported values are averages over at least three different trials. Values in parentheses are uncertainties determined from the standard error of the mean for the last digit of the reported rate constant. For EA in THF, the reported values include data from both EA in THF and EA/H₂O in THF

	100-fold excess TNT		100-fold excess amine			
base	$k_{\rm obs}~({\rm s}^{-1})~{\rm TNT}^-$	$k_{\rm obs}~(\rm s^{-1})~\rm TNT-OH^-/\rm TNT-B$	$k_{\rm obs}~(s^{-1})~{\rm TNT}^-$	$k_{\rm obs}~({\rm s}^{-1})~{\rm TNT-OH^-/TNT-B}$		
Reactions in THF						
EA	0.8(1)	0.0047(5)	5(1)	0.02(1)		
PA			4(2)	0.0027(9)		
BA	1.6(7)	0.0038(4)	4(2)	0.015(2)		
DEA	10(5)	0.0045(8)	2.0(5)	0.012(2)		
TEA	0.9(2)	0.0027(2)	1.1(4)	0.012(2)		
Reactions in MeOH						
EA	0.47(2)	0.005(2)	2.9(4)	0.008(3)		
PA	0.52(2)	0.02(2)	5.8(8)	0.014(7)		
BA	0.41(1)		3.9(4)	0.006(2)		
DEA	0.61(2)	0.02(2)	10(4)	0.0065(2)		
TEA	1.3(2)	0.014(8)	7(2)	0.024(4)		

Table 5. Thermodynamic Parameters for Each Explored Reaction between TNT and Bases Calculated at the B3LYP/6-31G*// $HF/6-311+G^{**}$ Level in Vacuum at T = 298.15 K (Data for the Calculations Are Given in Tables S3 and S4 in the Supporting Information)

reaction	$\Delta E_{\rm rxn}^{\circ}$ (kJ/mol)	$\Delta G^{\circ}_{ m rxn}$ (kJ/mol)	$\Delta H_{ m rxn}^{\circ}$ (kJ/mol)	$\Delta S^{\circ}_{ m rxn}$ (J mol ⁻¹ K ⁻¹)
$\rm TNT + OH^- \rightarrow \rm TNT^- + \rm H_2O$	-411.3	-412.4	-409.8	8.7
$\text{TNT} + \text{OH}^- \rightarrow \text{TNT} - \text{OH}^- \text{ C}_1$	-487.1	-435.6	-480.1	-149.2
$\text{TNT} + \text{OH}^- \rightarrow \text{TNT} - \text{OH}^- \text{ C}_3$	-460.7	-408.7	-453.1	-149.0
$\text{TNT} + \text{CH}_3\text{O}^- \rightarrow \text{TNT}^- + \text{CH}_3\text{OH}$	-293.8	-289.9	-286.1	12.8
$\text{TNT} + \text{CH}_3\text{O}^- \rightarrow \text{TNT} - \text{OCH}_3^- \text{C}_1$	-348.1	-281.6	-335.3	-180.2
$TNT + CH_3O^- \rightarrow TNT - OCH_3^- C_3$	-351.5	-283.4	-337.8	-182.4
$\text{TNT} + \text{NH}_3 \rightarrow \text{TNT}^- + \text{NH}_4^+$	487.3	499.3	495.1	-14.2
$\text{TNT} + \text{NH}_3 \rightarrow [\text{TNT}^-][\text{NH}_4^+]$	65.7	113.5	69.8	-146.5
$\text{TNT} + \text{NH}_3 \rightarrow \text{TNT} - \text{NH}_3 \text{ C}_1$	16.8	77.8	28.0	-167.0
$\text{TNT} + \text{NH}_3 \rightarrow \text{TNT} - \text{NH}_3 \text{ C}_3$	29.9	90.5	41.0	-165.8
$TNT + EA \rightarrow TNT^{-} + H^{+} - EA$	431.7	440.4	438.8	-5.5
$TNT + EA \rightarrow [TNT^{-}][H^{+}-EA]$	42.2	106.9	47.4	-199.5
TNT + EA \rightarrow TNT–EA $\rm C_1$	-6.1	68.0	4.4	-213.3
TNT + EA \rightarrow TNT–EA $\rm C_3$	6.9	81.4	17.7	-213.8
$TNT + DEA \rightarrow TNT^{-} + H^{+} - DEA$	391.0	399.8	398.0	-5.8
$\text{TNT} + \text{DEA} \rightarrow [\text{TNT}^{-}][\text{H}^{+}-\text{DEA}]$	23.5	94.0	29.1	-217.7
TNT + DEA \rightarrow TNT–DEA C_1	36.9	115.4	47.4	-227.8
TNT + DEA \rightarrow TNT–DEA C_3	30.1	108.4	40.2	-229.0
$TNT + TEA \rightarrow TNT^{-} + H^{+} - TEA$	371.8	381.8	380.0	-6.2
$TNT + TEA \rightarrow [TNT^{-}][H^{+}-TEA]$	56.1	128.6	63.8	-217.2

The deprotonation reactions with the amines are all calculated to be strongly disfavored, consistent with the experimental observations. When the product is allowed to form an ion pair, the electrostatic interaction reduces ΔE° , ΔG° , and ΔH° by more than 300 kJ/mol. The nucleophilic addition reactions are also disfavored for all of the amines. The nucleophilic addition and ion pair formation reactions have similar ΔG° values and are disfavored both enthalpically and entropically.

To assess the effect of solvation, the SM8 solvation model was used. Since this model assumes no change to the vibrational modes upon which the thermodynamic calculations rely,³⁸ it is possible to use only the energy changes to assess the

influence of a solvent. Figure 16 shows the energy change, $\Delta E_{\rm rxn,}$ for each explored TNT reaction as a function of solvent dielectric constant. The results again show the contrast between the anionic bases and the amine bases: as the dielectric constant increases, the reactions with hydroxide and methoxide ions become less favorable (but always still have $\Delta E_{\rm rxn} < 0$), while the reactions of TNT with amines become more favorable with increasing dielectric constant, with $\Delta E_{\rm rxn}$ becoming negative for most cases at high enough dielectric constant. In all cases, the proton transfer reaction is calculated to be energetically less favorable than nucleophilic addition.

The relative reactivities of hydroxide and methoxide are independent of solvation modeling, as the energy difference



Figure 16. ΔE_{rxn} plotted as a function of dielectric constant for TNT reactions with bases. The plots indicate the solvation dependence of TNT reactions with hydroxide, methoxide, and selected amines. The ordinate for each plot shows the reactants, and the legend for each plot shows the products. Energy calculations were performed at the B3LYP/6-31G*//HF/6-311+G** level of computation using the SM8 solvation model. Some points from the free ion computations at lower dielectric constant are off scale and thus have been omitted from this figure. It should be noted that the ΔE_{rxn} data for the methoxide adducts overlap such that the data points cannot be discerned. T = 298.15 K.

between the computed species remains similar for any dielectric constant. The C₁ TNT–OH⁻ adduct is predicted to be the more energetically favorable product. The TNT–OCH₃⁻ adduct isomers show very similar energies for all modeled dielectric constants, as the larger nucleophile is sterically hindered at the C₁ attack site. This also suggests kinetic hindrance of the adduct formation, as TNT⁻ is typically observed prior to the adduct's appearance.

To compare to experimental results, the $\Delta E_{\rm rxn}$ values calculated for TNT + OH⁻ in THF and MeOH were found to be the following: deprotonation in THF, -250.4 kJ/mol; deprotonation in MeOH, -132.3 kJ/mol; C1 σ adduct formation in THF, -310.5 kJ/mol; and C1 σ adduct formation in MeOH, -185.8 kJ/mol. Quantitatively, the calculated values are quite different than the ΔG° (which should be similar to, but not identical to, $\Delta E_{\rm rxn}$) values estimated from the rate constants for the competing reactions (-22 kJ/mol for deprotonation and -12 kJ/mol for σ adduct formation; Table 3). The differences can be attributed in part to the limitations of the solvation model used and to errors in the experimental parameters. In contrast, the calculations are successful in predicting that the extent of reaction should be significantly smaller in MeOH than in THF.

The NH_3 and EA products follow a similar trend, where the σ adduct formation reactions are of lower relative energy than the formation of an ion pair or free ions. The free ion formations are calculated to be the least energetically favorable, especially in solvents with low dielectric constants, which cannot stabilize the charges through electrostatic forces. In

addition, the change in relative energy for the NH₃ and EA σ adduct formations is about an order of magnitude less than for the hydroxide adducts in methanol ($\varepsilon = 33$). In vacuum, the computation indicates a nonfavorable reaction for the ammonia adduct and a barely favorable adduct formation with EA. This does not project well for the use of TNT/primary amine reactions for solid–vapor applications to detect TNT.

The size difference of DEA relative to EA changes the relative favorability of action as a Brønsted–Lowry base versus a nucleophile. The calculations predict the formation of the $[H^+-DEA][TNT^-]$ ion pair to be the most favorable reaction, with the free ions still more favorable than either σ adduct at dielectric constants higher than that of 1-propanol ($\epsilon = 20.1$). It is interesting to note that the C_3 carbon is expected to be the more energetically favorable addition site for the larger DEA nucleophile, but not by so much that we would not expect to see evidence of both adducts at equilibrium. Since TNT–TEA adducts did not converge because of the steric bulk of TEA, the only comparison to be made is that of TEA's capacity as a Brønsted–Lowry base. The TEA deprotonation reactions are not expected to be energetically favorable.

The calculations predict that the reaction of the amines may become favorable in solvents with a sufficiently large dielectric constant, but by only a few tens of kJ/mol. In contrast, even in solvents with high dielectric constants, the reaction between TNT and either hydroxide or methoxide is expected to be favorable by 100 kJ/mol or more. This implies that in any wet environment, where amines react with water to generate hydroxide, there is a significant energetic preference for TNT to

react with hydroxide rather than with the amine. This is consistent with experimental results.

CONCLUSION

We have shown through related ¹H NMR and visible absorbance spectroscopy, kinetic analysis, and computational modeling that amines do not play a direct role in the initial formation of decomposition products of TNT. Amines are not basic enough to directly deprotonate the methyl group of TNT. nor are they strong enough nucleophiles to compete with the small quantity of anionic species that they form through other acid/base reactions in solution. The reaction of an amine with water to generate hydroxide is required for a reaction with TNT to be observed, and then both deprotonation and σ adduct formation can be observed. The speciation in solution depends upon a combination of factors, including the specific base, the solvent, and the relative initial concentrations of reactants. When the base is hydroxide rather than an amine, the deprotonation reaction to give TNT⁻ is slightly more favorable in both THF and MeOH compared with formation of the σ adduct, TNT-OH-. For the amine bases, the primary component leading to the color change is TNT⁻, but the σ adducts, either TNT-OH⁻ or TNT-B, may be present in larger concentration.

The observation of visible-range absorbances, which are commonly used in sensor development, result from TNT⁻ or TNT-B depending on the solvent identity and water content. This finding may indicate the need for reassessment of existing sensors for better mechanistic clarification as well as caution regarding the choice of solvent in similar systems. Any sensor system using an amine transducer will operate under excess base conditions, which will require the presence of water to generate hydroxide to allow reaction. This implies that control of the humidity in a gas-phase sensor system will be important.

ASSOCIATED CONTENT

S Supporting Information

¹³C NMR spectra of TNT in THF- d_8 and CD₃OD; DEPT-135 spectra of TNT reacted with NaOD and then neutralized with DCl/D₂O; derivation of the kinetic model; UV–vis absorbance spectra as a function of time for all reactions between TNT and the different bases; and tabulated thermodynamic parameters of individual modeled reactants and products, including CT complexes, bases, and conjugate acids. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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