



Detection of dinitrotoluene isomers using reactions with bases: A structural, spectroscopic, kinetic, and computational study



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ARTICLE INFO

Article history:

Received 17 January 2015
Received in revised form 4 April 2015
Accepted 6 April 2015
Available online 20 April 2015

Keywords:

Dinitrotoluenes
Sigma complex
Thermodynamic calculations

ABSTRACT

The reactions of dinitrotoluenes (DNT) with hydroxide ion or wet alkylamines can be used to detect and identify each isomer. The reaction products give visible spectra that can be used directly to determine the isomer speciation with sensitivities in the low micromolar range. NMR spectroscopy in dimethylformamide provides unambiguous identification of the products of each DNT when the base is hydroxide. Kinetic studies show that the initial product of this reaction is the deprotonated anion followed by subsequent formation of σ -adducts and, in some cases, a dimer, with the exception of 2,4-DNT, which does not react beyond the acid–base reaction. Alkylamines do not react with any DNT, even when the amine is acting as the solvent, unless there is water present. Water is the limiting reagent in these cases, implying that in all cases the reacting species is the hydroxide ion, not the free amine. Computational studies are consistent with the inability of the alkylamine to deprotonate the methyl group in any of the DNT isomers. A general mechanism that is applicable to hydroxide and amine bases is proposed.

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1. Introduction

The study of nitroaromatic species has shown a resurgence in recent years because of the increased interest in the development of sensors for explosives [1–13], especially for trinitrotoluene (TNT). Different dinitrotoluene (DNT) isomers are a major impurity in military and industrial grade TNT. Although none of the DNT isomers can be used as explosives, their high volatility allows for more sensitive detection, which can ultimately be utilized in detection of TNT. Various methods have been proposed in the literature for detection of TNT. A common motif for these sensors is based on the reaction with amines [14–16], either directly or indirectly, such as displacement of an amine stabilizer around a quantum dot [17–23]. In addition to being easier to detect than TNT, the ratio of the various DNT isomers found in an explosive can be used to determine the origin of the material, which, for example, could be useful in identifying the manufacturer or country of origin of an IED.

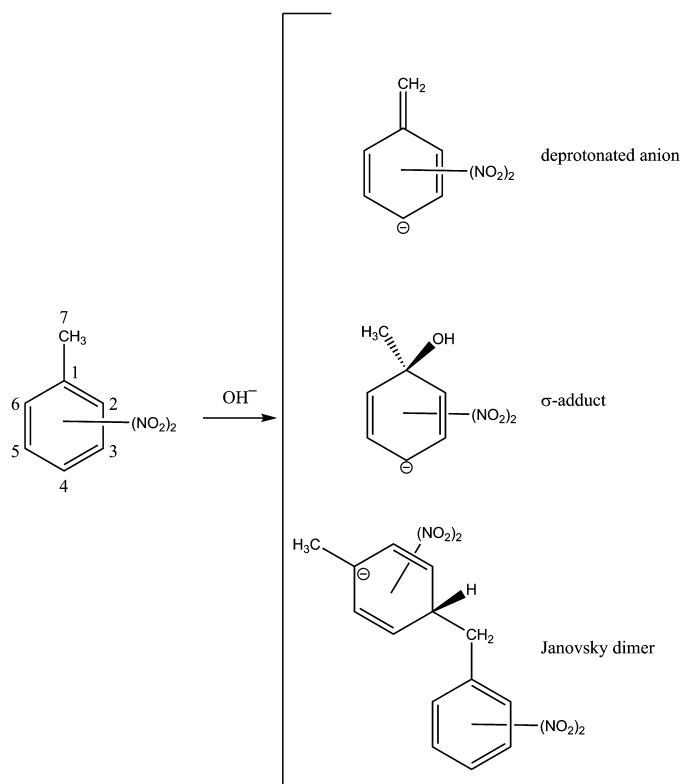
In addition to the practical applications, the study of the chemical reactivity of nitroaromatics is fascinating. Owing to the electron deficient nature of the ring, nucleophilic substitution on the ring is expected to be relatively facile. Indeed, anionic bases

are well known to add to trinitroaromatics to form σ -adducts or Meisenheimer complexes, with both experimental [24–38] and theoretical support [39–42]. Our previous work on TNT showed that nucleophiles ranging from hydroxide ion to amines and even to dimethylformamide (DMF) could lead to σ -adducts but that reaction conditions and solvation are important parameters in determining product speciation [43,44].

The presence of a methyl group on the nitroaromatic ring leads to an additional reaction pathway with bases, deprotonation. In fact, in a recent paper Olson et al. [45], warned “beware of the Meisenheimer trap” because 2,4-DNT in dimethylsulfoxide (DMSO) solvent reacted solely by deprotonation with no σ -adduct formation. Scheme 1 shows several possible reactions of DNTs when the base is hydroxide ion. Deprotonation of the methyl group [26,30], formation of a σ -adduct (shown in the 1-position, although addition to other positions on the ring is possible, in principle) [28,32,33,38], and dimerization have all been reported in the literature [25,27,29,30].

In this contribution we examine the reactivity of four isomers of DNT (2,3-DNT, 2,4-DNT, 3,4-DNT, and 2,6-DNT) with hydroxide ion in DMF and with alkylamines. We focus on alkylamines because these are what are used in sensor systems, typically bound to a substrate [14–16]. We use a combination of NMR spectroscopy to determine the structure of reaction products, visible spectroscopy to measure reaction kinetics, and quantum chemical calculations

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Scheme 1. Products of the reaction of DNT with hydroxide. DNT can be deprotonated at its methyl group forming the deprotonated anion, DNT^- , can have a nucleophilic addition to form a σ -adduct, DNT-1-OH^- , or can dimerize to form a Janovsky complex.

to support the interpretation of the experimental data. We confirm the finding of Olson et al. [45], that 2,4-DNT deprotonation of the methyl group is the only reaction observed. However, for 2,3-DNT, 2,6-DNT, and 3,4-DNT additional reactions occur. Formation of a σ -adduct at the 1-position is unequivocally identified by NMR spectroscopy for these three isomers when the base is hydroxide ion and the solvent is DMF. In addition, in sufficiently concentrated solutions, 2,3-DNT and 2,6-DNT form Janovsky dimers while 3,4-DNT does not show dimerization because of the blocked 4-position. For reaction with alkylamines we show that no reaction occurs with any of the DNT isomers unless there is water present, implying that the active species is the hydroxide ion, not the amine. In all cases, the deprotonated anion is an intermediate to subsequent reactivity. Finally, we propose a mechanism that can account for all of the observations.

2. Materials and methods

The only available isomers of DNT were obtained from Drs. Jimmie Oxley and James Smith and were used without further purification. The solvent used in this study, HPLC grade DMF (99.9%, inhibitor free), was purchased from Sigma–Aldrich and ACS reagent grade 0.1 M aqueous NaOH was purchased from Anachemia and both were used as received. Ethylamine (70% wt. ethylamine in water) (EA), propylamine (PA), and butylamine (BA) were purchased from Sigma–Aldrich.

NMR experiments were conducted in d_7 -DMF (99.5% D) purchased from Cambridge Isotope Laboratories. $\text{NaOD}/\text{D}_2\text{O}$ (40% w/w, 99.5% D) solution was purchased from Sigma–Aldrich. DNT solutions were quantitatively prepared, and ^1H spectra of the titration of $\text{NaOD}/\text{D}_2\text{O}$ in DNT solutions were acquired on a Bruker 300 MHz NMR spectrometer. The time delay from the addition of the base

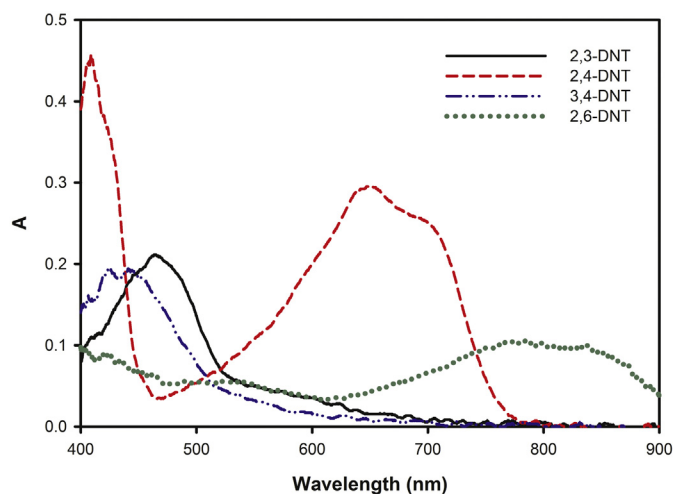


Fig. 1. Visible spectra of the reaction product of DNT with hydroxide ion in DMF solvent. Solid line, 2,3-DNT; dashed line, 2,4-DNT; dash-dotted line, 3,4-DNT; dotted line, 2,6-DNT. Each spectrum was chosen when the maximum value of the visible absorbance was observed after adding the base to the solution. In all cases the initial concentration of the DNT was 2.7×10^{-5} M.

to data acquisition was approximately 5 min per spectrum, due to solvent locking and shimming.

For the kinetic experiments using NaOH, solutions containing DNT were quantitatively prepared in DMF. These solutions were added to a cuvette and were equilibrated to 20.00 °C in a Peltier temperature controlled cuvette holder before and during the addition of the excess NaOH. A stock solution of NaOH was measured using a micropipette and added to the DNT solution such that the base was in 100-fold molar excess. For reactions with the amine bases, the base acted as the solvent, and a measured quantity of water was added to the cuvette (except for EA, which is supplied as a 70% solution in water) and then equilibrated to 25.00 °C. While stirring, a quantitative amount of solid DNT was added. Absorbance spectra were acquired using an Ocean Optics spectrometer with a tungsten-halogen lamp as the source. The wavelength resolution of the spectra was 1 nm and temporal resolution was 50 ms.

All quantum chemical computations were done using Spartan 10 software [46]. Structures of the neutral DNT, DNT^- , and DNT-1-OH^- σ -adduct for each isomer were done using density functional theory with the B3LYP functional and the 6-31G* basis set. To model DMF or H_2O solvation the SM8 model was used [47]. All structures converged with no imaginary frequencies except for 2,3-DNT-1- $\text{NH}_2\text{CH}_2\text{CH}_3$ and 3,4-DNT-1- $\text{NH}_2\text{CH}_2\text{CH}_3$ σ -adducts in vacuum.

3. Results and discussion

From our previous findings with TNT and as others have reported with DNTs, we expected that hydroxide would react readily with these compounds [5–7]. However, qualitative experiments conducted with measured quantity of DNTs in anhydrous aliphatic amines (propylamine (PA) and *n*-butylamine (BA)) as solvents showed no observable color change or other indication of reaction. In contrast, ethylamine (EA), which is supplied as a 70% solution in water, reacted quickly. When water was added to PA or BA reaction was noted.

3.1. Visible spectroscopy

Fig. 1 shows the visible spectra of the initial product of the reaction of each DNT with hydroxide in DMF solvent. In the case of 3,4-DNT the spectrum shown was collected after 55 s while for 2,3-DNT, 2,4-DNT, and 2,6-DNT the spectra taken after 15 s were

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