Density Functional Theory (DFT) Investigation of The Oxidative Degradation of NaAsO_2 Via Hydroxyl Radical

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Abstract

Arsenic is an environmentally ubiquitous health hazard due to its toxicity combined with its natural abundance and heavy industrial applications. Due to its role in cardiovascular disease, neurotoxicity, and various cancers, it is important to understand environmental fate of arsenic-containing compounds to take steps towards remediation. Sodium arsenite (NaAsO_2) is one such compound that has been used worldwide as an herbicide, rodenticide, and insecticide. It is also toxic by ingestion, inhalation, and skin absorption. In aqueous environments arsenite (As(III))-containing compounds can be oxidized to the less-toxic arsenate (As(V)) form. We have investigated the oxidation of sodium arsenite in water solution at the density functional theory level using the Minnesota 06 hybrid (M06-2X) functional and Pople basis sets (6-31G(d,p) and 6-311G(d,p)) with polarizable continuum model (PCM) solvation approach. Our computational results indicate that the oxidation mechanism of NaAsO_2 by hydroxyl radical proceeds via sequential addition reactions where sodium arsenite (III) converts to sodium arsenate (V) via an arsenic (IV) intermediate.

1.0 Introduction

Arsenic (As) is a plentiful element ranked 14th in abundance in seawater and 20th in the Earth's crust.[1–4] More than 320 naturally occurring minerals contain arsenic as the major component.[5] These As-enriched minerals include arsenates, arsinides, arsenites, sulfides, sulfo-salts, silicates, and oxides.[6] The primary source of As in the environment is actually found through natural desorption and dissolution of these minerals.[7–10] However, arsenic is also released into the environment through human vectors such as mining, coal combustion, wood preservatives, herbicides, fungicides, insecticides, and effluents from industrial sources.[5, 7, 8, 11]

There are four major valence states of As: arsenate (+5), arsenite (+3), arsenic (0), and arsine (-3).[12] The two most dominant species of arsenic found in natural environments are arsenate [As(V)] and arsenite [As(III)]. This is because arsenic rapidly oxidizes in oxygenated environments.[13] These cations readily associate with 3 or 4 oxygen atoms to form AsO_3^{3-} or AsO_4^{3-} . [13] These anionic states can also become protonated resulting in the acid forms: arsenous acid (H_3AsO_3) and arsenic acid (H_3AsO_4). [14] Arsenate is the most thermodynamically stable form in water. Arsenite is more commonly found in reduced redox environments.[15–17] Other forms of arsenic can be present in the environment such as monomethylarsonic acid, dimethylarsonic acid, arsenobentine, arsenocholine, arsenosugars, etc.[18, 19]

Arsenic has been identified as a Group I human carcinogen by the World Health Organization and is a highly toxic non-essential element that is often categorized alongside mercury, lead, and cadmium.[6, 20] Inorganic arsenic-containing compounds are generally more toxic than organic compounds and typically, As(III) is more toxic than As(V) . [21–23] Additionally, no chemical or biological pathways to degrade inorganic arsenics into harmless small molecules exist. They can be transformed into other compounds that are less toxic than their parent compounds.[14] Remediation of arsenics from groundwater often involve oxidation, adsorption, coagulation-flocculation, ion-exchange, and membrane processes.[24]

It has been reported that As(V) containing compounds react preferentially with Al^{3+} , Fe^{3+} , Mn^{2+} , and Mn^{4+} containing compounds that can often be found as metal oxides in sediment deposits.[13] Arsenate containing compounds have been shown to be removed in some amounts from aquatic environments via soil adsorption.[25] Therefore, in addition to being generally less toxic, As(V) is shown to be less mobile than As(III) in regards to water transport.[3] It is for this reason that much attention has been drawn to the oxidation of As(III) compared to As(V).[9, 26, 27]

Of the As(III) containing compounds, arsenous acid (H_3AsO_3) is one of the most widely studied compounds.[14] It has been shown that H_3AsO_3 can be oxidized to H_3AsO_4 utilizing ozone, molecular oxygen, activated H_2O_2 , photochemical oxidation, permanganate, Mn(III/IV) oxide, iron oxides, and ferrate, among others.[14] It has been reported that the oxidation of As(III) proceeds through the formation of an unstable As(IV) complex before achieving the As(V) oxidation state.[28]

While arsenite containing compounds can be readily oxidized to the less toxic arsenate compounds; computational studies have focused on arsenous acid and its anion (AsO_3^{3-}). Sodium arsenite (NaAsO_2) is another arsenite-containing compound that has been used as an herbicide, rodenticide, and insecticide; however, little has been published with regards to the oxidation of NaAsO_2 . [9, 14, 29] However, a rate constant for the oxidation of the arsenite anion from this compound by hydroxyl radical ($\text{OH}^\bullet + \text{AsO}_2^- \rightarrow \text{As(IV)}$) was found to be $9.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. [30, 31] In order to investigate this process and compare to available experimental data we have performed density functional theory calculations to determine the mechanism of oxidation for sodium arsenite via hydroxyl radical.

2.0 Computational Methods

Gaussian16[32] was used to carry out quantum mechanical calculations of the reaction mechanisms of the transformation of sodium arsenite to sodium arsenate through an arsenic (IV) intermediate state (Scheme I).

Scheme I

Density functional theory calculations were performed using the Minnesota 06 hybrid functional (M06-2X)[33] with the 6-31G(d,p)[34–39] and 6-311G(d,p)[39–42] basis sets. Effect of water solvation was considered using the polarizable continuum model (PCM) with the default parameters for water ($\epsilon = 78.3553$) as available in Gaussian16.[43, 44] Harmonic vibrational frequencies were used to determine that structures resided at either a minima or transition state on the potential energy surface as indicated by the presence of no imaginary frequencies or one imaginary frequency, respectively. The Synchronous Transit-Guided Quasi-Newton (STQN) Method[45, 46] was used as necessary to search for transition states using the QST2 and QST3 keywords in addition to manual potential energy scans. The QST2 method uses the reactant and product geometries alone as input to attempt to search for the transition

state. The QST3 method uses the reactant and product geometries as well as an initial guess geometry for the transition state to attempt to search for the transition state.

3.0 Results & Discussion

Initial optimizations of the reactant structures NaAsO_2 and $\text{OH}^\bullet$ were performed separately to obtain starting geometries. These structures were then combined, with the two molecules placed approximately 3.00 Å apart (distance measured between the arsenic of the NaAsO_2 and the oxygen of the $\text{OH}^\bullet$). The combined structures were then allowed to relax to obtain a starting orientation of the molecules. However, upon optimization the hydroxyl group immediately moved to within bonding distance (1.79 Å) of the As atom of the arsenite complex.

We then performed a relaxed potential energy scan of the bond between the arsenic and the hydroxyl radical. Our calculations showed a continual increase in potential energy as the hydroxyl group was pulled away from the arsenic, breaking the As-OH bond, with no definitive peaks to indicate a potential transition state (Figure S1). The procedure of pulling the intermediate or product of a reaction apart is sometimes easier in cases where the intermediate or product are more stable than the reactant and there is a little to no activation barrier between the two.

Explicit water molecules were added to stabilize the hydroxyl radical in a starting configuration where the reactants were at least 3.00 Å apart. Initial attempts were made with two explicit water molecules to save computational time, but the results were very similar to the calculations with no explicit water molecules. A recent study on H_3AsO_3 oxidation by $\text{OH}^\bullet$ used four water molecules to create a hydrogen bonding around the complex[28], which we decided to adopt for our system (Figure 1a).

We performed a relaxed potential energy scan of the As-OH bond formation (Figure 2a). We again found that the product appears to rapidly form with no clear indication of a transition state in the potential energy surface. We do see a large drop in energy in the reaction coordinate points surrounding ~2.18 Å. However, this drop in energy appears to be a result of slight movements of the atoms as the $\text{OH}^\bullet$ begins to coordinate in closer proximity to the As atom. We attempted to optimize the structure to a transition state using opt=TS on data points surrounding this region, but all attempts resulted to the product structure with no imaginary frequencies and thus no transition state was found. Therefore, our data suggests that when in close proximity to $\text{OH}^\bullet$ the initial oxidation step of NaAsO_2 is a barrierless process.

A second hydroxyl radical was then added to the system along with a fifth explicit water molecule (Figure 1b). Optimizations for this system began with the hydroxyl radical roughly 3.00 Å away from the intermediate As(IV) complex. The optimization proceeded directly to the product with a bond forming between the hydroxyl radical and the arsenic. We then attempted a relaxed scan of the potential energy surface by breaking the bond between the As and the oxygen atom of the second hydroxyl radical (Figure 2b).

The potential energy scans did show a small peak around 2.20 Å which could have been indicative of a transition state. However, upon close inspection of the structures from the relaxed scans it was discovered that this small increase and subsequent drop in the potential energy surface is a result of changes in the hydrogen bonding network which resulted in water molecules moving to other parts of the system (Figure S2). Attempts were made to perform transition state calculations on the structures found at the peak and on either side of the peak. However, attempts to optimize a transition state (opt=TS) resulted in the final As(V) product. The resulting structure also had no imaginary frequencies indicating the structure found was a minima and not a transition state. The structure on the left side of the peak was used as the reactant structure along with the optimized product in a QST2 calculation to search for the elusive transition state; however, these calculations either failed to optimize or optimized to the As(V) product (NaH_2AsO_4). Finally, QST3 calculations were performed using the data used for the QST2 for the reactant and product input and the guess for the transition state was taken from the highest point on the peak. These calculations also optimized to the product with no imaginary frequencies rather than a transition state.

These results indicate that this oxidation step may also proceed as a barrierless addition of hydroxyl radical to the arsenic (IV) intermediate to form the arsenate (V) product. However, to determine if increasing solvation would stabilize a potential transition state, we performed a test calculation with double the amount of explicit water molecules. We performed a potential energy scan identical to the one shown in Figure 2b, but included ten water molecules (Figure 1c & Figure 2c).

The PES shows a much smoother curve from 1.70 Å to 2.20 Å with no indication of the peaks found in the previous calculation with only five explicit waters. However, we do see a similar peak near 2.33 Å when the 6-311G(d,p) basis set was used. It was at this point in this calculation that the sodium atom moved to the other side of the molecule and in subsequent steps a bond began to form between the arsenic and the oxygen of another water molecule. Further optimization of this structure revealed a bond between this water and the arsenic complex accompanied by another series of protonation/deprotonation events. The water bonding to the arsenic lost its proton to another water, which caused a domino effect of protons being transferred between water molecules until the originally designated hydroxyl radical was protonated and thus transformed into a water molecule. Overall, this shows that it is highly preferential for this oxidation to occur even if it must happen by implicating the hydrogen bond network of waters.

4.0 Conclusions

Our results suggest that the oxidation reaction proceeds via a barrierless addition of sodium arsenite (III) with $\text{OH}^\bullet$ to form an intermediate As(IV) complex ($\text{NaHAsO}_3^\bullet$). This As(IV) intermediate is then further oxidized to sodium arsenate (V) through a second barrierless addition of $\text{OH}^\bullet$. While information on the exact mechanism to our knowledge is lacking, it appears that this barrierless reaction is in line with the general statement in the literature which is that arsenite compounds can be readily oxidized to arsenates.

[14] Additionally the published rate constant for the anion ($\text{OH}^\bullet + \text{AsO}_2^- \rightleftharpoons \text{As(IV)}$), $9.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, indicates that the reaction happens very fast which further supports a barrierless reaction process.[30, 31]

Declarations

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Availability of Data and Material. The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code Availability. Not applicable.

Author Contributions. All authors contributed to the study conception and design. Computations, data collection and analysis were performed by Ashlyn M. Koval. The first draft of the manuscript was written by Ashlyn M. Koval and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Figures

Figure 1

Structures taken from the relaxed potential energy scans of the oxidation of sodium arsenite by the addition of hydroxyl radicals at the M06-2X/6-311G(d,p) level of theory. The atoms involved in the reaction are shown in the ball and stick model and the explicitly calculated solvent molecules are shown in tube model. Arsenic is shown in brown, oxygen in red, hydrogen in white, and sodium in pink. Implicit solvation was accounted for using the PCM approach with default parameters for water in Gaussian16. **(a)** The optimized structure of the sodium arsenic (IV) intermediate after oxidation by one hydroxyl radical shown with four explicit solvent molecules. **(b)** The optimized structure of the sodium arsenate product after oxidation by the second hydroxyl including with five explicit solvent molecules. **(c)** The optimized structure of sodium arsenate product after oxidation by the second hydroxyl including ten explicit solvent molecules

Figure 2

Relative potential energy change in response As-OH bond formation utilizing M06-2X/6-31G(d,p) and M06-2X/6-311G(d,p). Geometry was allowed to relax at each step. Implicit solvation was accounted for using the PCM approach with default parameters for water in Gaussian16. Individual reaction conditions as follows: **(a)** First addition of OH⁻ with formation of the As-OH bond in figure 1a using four explicit water molecules arranged within hydrogen bonding distance to the reactants. **(b)** Second addition of OH⁻ and formation of the As-OH bond in figure 1b using five explicit water molecules arranged within hydrogen bonding distance to the reactants. **(c)** Second addition of OH⁻ and formation of the As-OH bond in figure 1c using ten explicit water molecules arranged within hydrogen bonding distance to the reactants.

Supplementary Files

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