Density Functional Theory (DFT) Investigation of The Oxidative Degradation of NaAsO$_2$ Via Hydroxyl Radical

Ashlyn M Koval (Ashley.M.Koval@erdc.dren.mil)
Simetri Inc.
https://orcid.org/0000-0003-4189-3880

Harley McAlexander
ERDC: US Army Engineer Research and Development Center

Christa M. Woodley
ERDC: US Army Engineer Research and Development Center

Manoj K. Shukla
ERDC: US Army Engineer Research and Development Center
https://orcid.org/0000-0002-7560-1172

Research Article

Keywords: Arsenic, Sodium Arsenite, Oxidation, Hydroxyl Radical

Posted Date: December 30th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-1178704/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License

Version of Record: A version of this preprint was published at Structural Chemistry on January 31st, 2022. See the published version at https://doi.org/10.1007/s11224-022-01884-5.
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$_3$AsO$_3$) and arsenic acid (H$_3$AsO$_4$).[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, arsenobentaine, 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_{3}AsO_{3}) is one of the most widely studied compounds.[14] It has been shown that H_{3}AsO_{3} can be oxidized to H_{3}AsO_{4} utilizing ozone, molecular oxygen, activated H_{2}O_{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 (OH• + AsO_{2}^{−} → As(IV)) was found to be 9.0 x 10^{9} L mol^{-1} 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

NaAsO_{2} + OH• → NaHAsO_{3}^{−} + OH^{−} → NaH_{2}AsO_{4}^{−}

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 (ε = 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
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 OH$^-$ 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 OH$^-$). 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$_3$AsO$_3$ oxidation by OH$^-$ used four water molecules to create a hydrogen bonding around the complex\cite{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 OH$^-$ 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 OH$^-$ 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$_2$AsO$_4$). 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 OH$^-$ to form an intermediate As(IV) complex (NaHAsO$_3$•). This As(IV) intermediate is then further oxidized to sodium arsenate (V) through a second barrierless addition of OH$^-$. 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.
Additionally the published rate constant for the anion ($\text{OH}^+ + \text{AsO}_2^- \rightarrow \text{As(IV)}$), $9.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, indicates that the reaction happens very fast which further supports a barrierless reaction process.[30, 31]

## Declarations

### 5.0 Acknowledgements

The authors would like to thank Dr. Caitlin Bresnahan and Dr. Robert Lamb for providing feedback and guidance on the reaction mechanism calculations. The use of trade, product, or firm names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Government. The tests described and the resulting data presented herein, unless otherwise noted, were obtained from research funded under the Installations and Operational Environments, Office of the Technical Director of the United States Army Corps of Engineers, and the Environmental Security Technology Certification Program of the Department of Defense by the USAERDC. Permission was granted by the Chief of Engineers to publish this information. The findings of this report are not to be considered as an official Department of the Army position unless so designated by other authorized documents. This work was supported by a grant of computer time from the DoD High Performance Computing Modernization Program at ERDC, Vicksburg, MS. This document has been approved for public release (Distribution Statement A) by the Engineer Research and Development Center.

### 6.0 Statements and Declarations

**Funding.** The tests described and the resulting data presented herein, unless otherwise noted, were obtained from research funded under the Installations and Operational Environments, Office of the Technical Director of the United States Army Corps of Engineers, and the Environmental Security Technology Certification Program of the Department of Defense by the USAERDC. This work was supported by a grant of computer time from the DoD High Performance Computing Modernization Program at ERDC, Vicksburg, MS.

**Conflicts of Interest/Competing Interests.** The authors have no relevant financial or non-financial interests to disclose.

**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.
References

1. Mandal BK, Suzuki KT (2002) Arsenic round the world: a review. Talanta 58:201–235. https://doi.org/10.1016/S0039-9140(02)00268-0

2. Flora SJS (2015) Arsenic: Chemistry, Occurrence, and Exposure. In: Handbook of Arsenic Toxicology. Elsevier, pp 1–49

3. Hassan MM (2018) Arsenic in Groundwater: Poisoning and Risk Assessment, 1st edn. CRC Press, Boca Raton

4. Ravenscroft P, Brammer H, Richards K (2009) Arsenic Pollution: A Global Synthesis. Wiley-Blackwell, Oxford

5. US EPA (2002) Arsenic treatment technologies for solid, waste, and water

6. Ghosh (Nath) S, Debsarkar A, Dutta A (2019) Technology alternatives for decontamination of arsenic-rich groundwater—A critical review. Environmental Technology and Innovation 13:277–303. https://doi.org/10.1016/j.eti.2018.12.003

7. Mondal P, Majumder CB, Mohanty B (2006) Laboratory based approaches for arsenic remediation from contaminated water: Recent developments. J Hazard Mater 137:464–479. https://doi.org/10.1016/j.jhazmat.2006.02.023

8. Bundschuh J, Bhattacharya P, Sracek O et al (2011) Arsenic removal from groundwater of the Chaco-Pampean Plain (Argentina) using natural geological materials as adsorbents. Journal of Environmental Science Health Part A 46:1297–1310. https://doi.org/10.1080/10980115.2011.598838

9. Singh R, Singh S, Parihar P et al (2015) Arsenic contamination, consequences and remediation techniques: A review. Ecotoxicol Environ Saf 112:247–270. https://doi.org/10.1016/j.ecoenv.2014.10.009

10. Han L, Gao B, Hao H et al (2019) Arsenic pollution of sediments in China: An assessment by geochemical baseline. Sci Total Environ 651:1983–1991. https://doi.org/10.1016/j.scitotenv.2018.09.381

11. Chowdhury S, Mazumder MAJ, Al-Attas O, Husain T (2016) Heavy metals in drinking water: Occurrences, implications, and future needs in developing countries. Sci Total Environ 569–570:476–488. https://doi.org/10.1016/j.scitotenv.2016.06.166

12. Tamaki S, Frankenberger WT (1992) Environmental Biochemistry of Arsenic. In: Reviews of Environmental Contamination and Toxicology. pp 79–110

13. Naidu R, Smith E, Owens G et al (2006) Managing Arsenic in the Environment: From Soil to Human Health. CSIRO publishing, Collingwood Australia

14. Wang Z, Fu Y, Wang L (2021) Abiotic oxidation of arsenite in natural and engineered systems: Mechanisms and related controversies over the last two decades (1999–2020). J Hazard Mater 414:125488. https://doi.org/10.1016/j.jhazmat.2021.125488
15. Sharma VK, Sohn M (2009) Aquatic arsenic: Toxicity, speciation, transformations, and remediation. Environ Int 35:743–759. https://doi.org/10.1016/j.envint.2009.01.005

16. Zhao F-J, McGrath SP, Meharg AA (2010) Arsenic as a food chain contaminant: Mechanisms of plant uptake and metabolism and mitigation strategies. Annu Rev Plant Biol 61:535–559. https://doi.org/10.1146/annurev-arplant-042809-112152

17. Gupta DK, Srivastava S, Huang HG et al (2011) Arsenic Tolerance and Detoxification Mechanisms in Plants. In: Sherameti I, Varma A (eds) Detoxification of Heavy Metals. Springer, Berlin, pp 169–179

18. Tangahu BV, Sheikh Abdullah SR, Basri H et al (2011) A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. International Journal of Chemical Engineering 1–31. https://doi.org/10.1155/2011/939161

19. Smith AH, Goycolea M, Haque R, Biggs ML (1998) Marked increase in bladder and lung cancer mortality in a region of northern chile due to arsenic in drinking water. Am J Epidemiol 147:660–669. https://doi.org/10.1093/oxfordjournals.aje.a009507

20. van Halem D, Bakker SA, Amy GL, van Dijk JC (2009) Arsenic in drinking water: a worldwide water quality concern for water supply companies. Drinking Water Engineering Science 2:29–34. https://doi.org/10.5194/dwes-2-29-2009

21. Abedin MdJ, Cresser MS, Meharg AA et al (2002) Arsenic accumulation and metabolism in rice (Oryza sativa L.). Environmental Science Technology 36:962–968. https://doi.org/10.1021/es0101678

22. Abedin MJ, Feldmann J, Meharg AA (2002) Uptake kinetics of arsenic species in rice plants. Plant Physiol 128:1120–1128. https://doi.org/10.1104/pp.010733

23. Schat H, Llugany M, Vooijs R et al (2002) The role of phytochelatins in constitutive and adaptive heavy metal tolerances in hyperaccumulator and non-hyperaccumulator metallophytes. J Exp Bot 53:2381–2392. https://doi.org/10.1093/jxb/erf107

24. Mondal P, Bhowmick S, Chatterjee D et al (2013) Remediation of inorganic arsenic in groundwater for safe water supply: A critical assessment of technological solutions. Chemosphere 92:157–170. https://doi.org/10.1016/j.chemosphere.2013.01.097

25. Suda A, Makino T (2016) Functional effects of manganese and iron oxides on the dynamics of trace elements in soils with a special focus on arsenic and cadmium: A review. Geoderma 270:68–75. https://doi.org/10.1016/j.geoderma.2015.12.017

26. Hug SJ, Canonica L, Wegelin M et al (2001) Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters. Environmental Science Technology 35:2114–2121. https://doi.org/10.1021/es001551s

27. Wang Z, Bush RT, Liu J (2013) Arsenic(III) and iron(II) co-oxidation by oxygen and hydrogen peroxide: Divergent reactions in the presence of organic ligands. Chemosphere 93:1936–1941. https://doi.org/10.1016/j.chemosphere.2013.06.076

28. Masliy AN, Kuznetsov AM, Korshin GV (2020) The intrinsic mechanism of catalytic oxidation of arsenite by hydroxyl-radicals in the H_{3}AsO_{3}^{2−}/HCO_{3}^{−}−H_{2}O system: A quantum-chemical
examination. Chemosphere 238:124466. https://doi.org/10.1016/j.chemosphere.2019.124466

29. National Center for Biotechnology Information PubChem Compound Summary for CID 443495, Sodium arsenite. https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-arsenite. Accessed 29 Nov 2021

30. Buxton G, Greenstock CL, Helman WP, Ross AB (1988) Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (\cdot OH/\cdot O\textsuperscript{−}) in aqueous solution. J Phys Chem Ref Data 17:513–886. https://doi.org/10.1063/1.555805

31. Adams GE, Boag JW, Michael BD (1965) Reactions of the hydroxyl radical. Part 2.—Determination of absolute rate constants. Trans Faraday Soc 61:1417–1424. https://doi.org/10.1039/TF9656101417

32. Frisch MJ, Trucks GW, Schlegel HB et al (2016) Gaussian 16, Revision A.03

33. Zhao Y, Truhlar DG (2008) The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. Theoret Chem Acc 120:215–241. https://doi.org/10.1007/s00214-007-0310-x

34. Ditchfield R, Hehre WJ, Pople JA (1971) Self-consistent molecular-orbital methods. IX. An extended Gaussian-type basis for molecular-orbital studies of organic molecules. J Chem Phys 54:724–728. https://doi.org/10.1063/1.1674902

35. Hehre WJ, Ditchfield R, Pople JA (1972) Self—consistent molecular orbital methods. XII. Further extensions of Gaussian—type basis sets for use in molecular orbital studies of organic molecules. J Chem Phys 56:2257–2261. https://doi.org/10.1063/1.1677527

36. Hariharan PC, Pople JA (1973) The influence of polarization functions on molecular orbital hydrogenation energies. Theoret Chim Acta 28:213–222. https://doi.org/10.1007/BF00533485

37. Francl MM, Pietro WJ, Hehre WJ et al (1982) Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. J Chem Phys 77:3654–3665. https://doi.org/10.1063/1.444267

38. Rassolov VA, Ratner MA, Pople JA et al (2001) 6-31G* basis set for third-row atoms. J Comput Chem 22:976–984. https://doi.org/10.1002/jcc.1058

39. Binning RC, Curtiss LA (1990) Compact contracted basis sets for third-row atoms: Ga-Kr. J Comput Chem 11:1206–1216. https://doi.org/10.1002/jcc.540111013

40. Curtiss LA, McGrath MP, Blaudeau JP et al (1995) Extension of Gaussian-2 theory to molecules containing third-row atoms Ga-Kr. J Chem Phys 103:6104–6113. https://doi.org/10.1063/1.470438

41. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. J Chem Phys 72:650–654. https://doi.org/10.1063/1.438955

42. McLean AD, Chandler GS (1980) Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, \( Z =11–18 \). J Chem Phys 72:5639–5648. https://doi.org/10.1063/1.438980
43. Miertuš S, Scrocco E, Tomasi J (1981) Electrostatic interaction of a solute with a continuum. A direct utilization of AB initio molecular potentials for the prevision of solvent effects. Chem Phys 55:117–129. https://doi.org/10.1016/0301-0104(81)85090-2

44. Tomasi J, Mennucci B, Cammi R (2005) Quantum Mechanical Continuum Solvation Models. Chem Rev 105:2999–3094. https://doi.org/10.1021/cr9904009

45. Peng C, Bernhard Schlegel H (1993) Combining Synchronous Transit and Quasi-Newton methods to find transition states. Isr J Chem 33:449–454. https://doi.org/10.1002/ijch.199300051

46. Peng C, Ayala PY, Schlegel HB, Frisch MJ (1996) Using redundant internal coordinates to optimize equilibrium geometries and transition states. J Comput Chem 17:49–56. https://doi.org/10.1002/(SICI)1096-987X(19960115)17:1<49::AID-JCC5>3.0.CO;2-0

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

This is a list of supplementary files associated with this preprint. Click to download.

- SodiumArsenitePaperSIAK20211103.docx