PHOSPHONOSULFONATE(3-) $O_3PSO_3^{3-}$ AND RELATED IONS

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The ions dithionate $S_2O_6^{2-}$ and hypophosphate $P_2O_6^{4-}$ are well known. However the isoelectronic phosphonosulfonate(3-) ion $O_3PSO_3^{3-}$ is not. Neither is the isoelectronic $O_3SClO_6^-$ ion. Previous experimental study of the oxidation of thiophosphate ion O_3PS^{3-} suggested the formation of $O_3PSO_3^{3-}$ but the conclusion remains tentative. (1) In the present study, HF/6-31G and HF/6-31G(d) molecular orbital calculations were carried out for each of the four ions, both in the gas phase and solvated in aqueous solution. With Jaguar 4, geometries were optimized for both gas phase and solvated structures for the four ions. In the gas phase in HF/6-31G, Jaguar 4 and Gaussian (94 or 98W) show stable structures for $P_2O_6^{4-}$, $S_2O_6^{2-}$, and $O_3SClO_6^-$, while gas phase $O_3PSO_3^{3-}$ is calculated to dissociate to planar PO_3^- and pyramidal SO_3^{2-}. However solvated (aqueous) $O_3PSO_3^{3-}$ is calculated by Jaguar 4 to be stable in HF/6-31G, though with a slightly long S-P bond length of 258 pm, compared with 230 pm for S-S in solvated $S_2O_6^{2-}$ and 219 pm for P-P in solvated $P_2O_6^{4-}$. In HF/6-31G solvation also shortens the central X-Y bond in $P_2O_6^{4-}$ and $S_2O_6^{2-}$ but lengthens it in $O_3SClO_6^-$. Next in HF/6-31G(d) and DFT B3LYP/6-31G(d), all four ions are calculated to be stable both in the gas phase and in solution. Vibrational frequencies and infrared intensities have been calculated in HF/631G(d) and DFT B3LYP/6-31G(d) for the normal modes of vibration of the four ions, both gas phase and solvated. Gas phase Raman intensities have been calculated in HF/6-31G(d). Thus calculations indicate that the phosphonosulfonate ion(3-) $O_3PSO_3^{3-}$ is stabilized by solvation in HF/6-31G, while all four ions are stable in HF/631G(d) and DFT B3LYP/6-31G(d), both gas phase and solvated.. Further investigation of protonated species is planned.

References:

1. Arlen Viste and Jeanne Pfaff, "Oxidation of Thiophosphate," *Proc. S.D. Acad. Sci.*, ***70***, 262-263 (1991). Abstract.