Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Reactivity, vibrational spectroscopy, internal rotation and thermochemical aspects of methylarsine

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ARTICLE INFO

ABSTRACT

The aim of this investigation was to perform a characterization of the spectroscopic and thermodynamic properties of methylarsine (CH_3AsH_2). Post-Hartree-Fock, 29 DFT methods and eight different composite methodologies were employed in these analyses. A comparison between harmonic and anharmonic frequency accuracies in reproducing the observable frequencies was performed here. In addition, the $CH_3AsH_2 \rightarrow CH_2AsH_3$ isomerization barrier energy was estimated in 100 kcal mol^{-1}, whereas the H_2-release routes barrier heights were in the 45–107 kcal mol^{-1} range. A rate constant of 10^{-66} s^{-1} was predicted regarding the isomerization route, while the CH_2AsH_3 hydrogen elimination mechanism is faster than the methylarsine one. The transition state structure of the CH_3AsH_2 internal rotational barrier energy varied between 1.0 and 1.4 kcal mol^{-1}. For the CH_2AsH_3 internal rotation the estimated barrier heights varied 0.6–2.5 kcal mol^{-1}. The adiabatic ionization energy and the heat of formation each structure was also calculated here.

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1. Introduction

Methylarsine (CH_3AsH_2) is one of the major volatile organoarsenic compounds which can be detected in environmental and biological samples [1–8]. Due to the numerous implications of arsenic compounds, CH_3AsH_2 has been focus of many different investigations involved in the development of new extraction and detection analytical methodologies [1–8], as in the synthesis of different metal complexes [9–13]. Nevertheless, through the years there have been only a few studies that have performed a spectroscopic or even a thermodynamic characterization of methylarsine [14–18], which is a different picture when compared to the several investigations of its nitrogen [19–24] and phosphorous analogues [25–32]. In 2009, Kim et al. [18] reported an analysis of the harmonic vibrational modes of methylarsine, and also an investigation of its potential surface energy, where several properties with the MP2 method employing the 6-311G(d,p) basis sets were predicted by the authors. In addition to the study of Kim and co-authors [18], the other investigations were related to the CH_3AsH_2 internal rotational barrier, which were performed between 1960 and 1969 based on the infrared spectra analysis [15,16].

The purpose of this study is to perform a quantum mechanical analysis of methylarsine and its isomer, CH_2AsH_3, in order to investigate and to understand the electronic, spectroscopic and thermodynamic properties of this molecule. In this investigation the following aspects will

be predicted: (a) the geometric parameters and the vibrational frequencies; (b) a characterization of the ionization potential; (c) the calculation of the heat of formation; (d) an analysis of the pathways associated with the unimolecular arrangement, with the hydrogen release routes and those related to the internal rotational barriers; (e) as well as insights into other electronic properties from the Quantum Theory of Atoms in Molecules (QTAIM) [33] and the Natural Bond Orbital Theory (NBO) analysis. In addition, several of these previous analyses performed for methylarsine were also devoted to its isomer, CH_2AsH_3 (see Fig. 1)

2. Methodology

All the calculations were carried out with Gaussian 09 program [34]. Stationary points on the potential energy surface of the reaction system were fully optimized, followed by evaluating harmonic vibration frequencies to characterize their nature as minima or first-order saddle points. The geometries of the reactant, product, and the transition state structures (TS) were fully optimized with the aid of analytical gradients using the Berny algorithm with redundant internal coordinates until a stationary point on the potential surface is found [35–37]. Stationary points on the potential surface corresponding to first order saddle points were verified by means of a normal mode analysis that yielded a single imaginary frequency related to the reaction path. The intrinsic reaction coordinate (IRC) was calculated in order to follow the reaction path [38,39].

Several methodologies were employed such as CCSD(T) [40], QCISD(T) [40], QCISD [41,42], MP2 [43,44] and CASSCF [45,46] and

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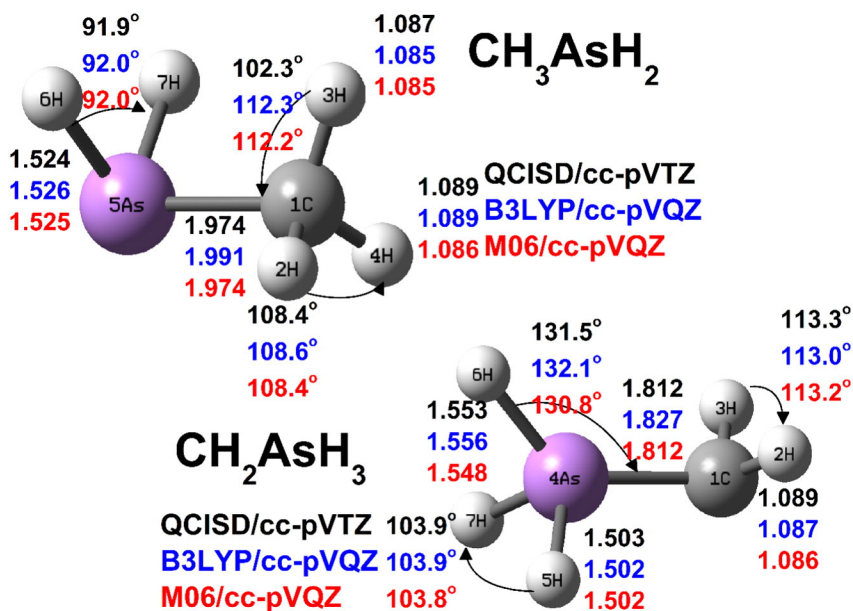E-mail address: rommelbv@yahoo.com.br.

Fig. 1. CH$_3$AsH$_2$ and CH$_2$AsH$_3$ optimized structures. Bond lengths (in Å) and angles (in °) obtained with QCISD/cc-pVTZ, B3LYP/cc-pVQZ and M06/cc-pVQZ methods.

different Density Functional Theory methods. In the case of DFT methods, twenty-nine different functionals were carried out, including the generalized gradient approximation (GGA), hybrid-GGA, meta-hybrid-GGA and meta-GGA, as well as several functionals with the empirical London dispersion corrections: TPSSh [47], O3LYP [48], tHCTHhyb [49], B3PW91 [50,51], B3LYP [50,52], B3P86 [50,53], B97-1 [54], B97-2 [55], B98 [56], PBE1PBE [57,58], X3LYP [59], M06 [60], M05 [61], BMK [62], M06-2X [63], M05-2X [63], BHandH [64], BHandHLYP [64], M06-HF [65], wB97 [66], wB97X [66], wB97XD [67], CAM-B3LYP [68], LC-wPBE [69,70], B97D [71], M06L [64], BP86 [53], BPW91 [51] and B2P-LYP [72]. Different basis sets were applied in these simulations, such as 6-31G(2df,2pd) [73,74], 6-31G(3df,3pd) [73,74], 6-311++G(3df,3pd) [73,74], cc-pVnZ (n = T,Q) [75–77], aug-cc-pVnZ (n = T,Q) [75–77], pcseg-2 [78] and Def2-TZVP [79]. The cc-pwCVTZ-PP basis set [80] was used with the objective of evaluating the effect of a pseudo-potential for the arsenic atom, whereas cc-pVTZ was employed for the other elements. The composite following methods were also carried out: CBS-4M [81,82], CBS-QB3 [83,84], G3 [85], G3MP2 [86], G3B3 [85], G3MP2B3 [86], G4 [87] and G4MP2 [88].

In the calculation of the heat of formation the methodology proposed by Curtis et al. [89] was applied, which involves a combination of experimental and calculated values. For the total atomization energy, the heats of formation at 0 K for the elements were provided by NIST-JANAF [90]: C (ΔH_f^{0K} = 169.68 kcal mol^{-1}), and H (ΔH_f^{0K} = 58.99 kcal mol^{-1}). For arsenic, the heat of formation value recommended by Mok et al. [91] was used (ΔH_f^{0K} = 70.30 kcal mol^{-1}). The carbon spin-orbit correction was obtained from Moore [92]. For the enthalpy correction of the arsenic element the calculated value of 1.00 kcal mol^{-1} was attributed, due to the absence of an experimental value.

In the case on the reaction pathways (reactants, products and TSs), each structure was optimized with QCISD/cc-pVTZ. The energy refinements were carried out at the CCSD(T) level of theory with the two-point extrapolation formula of Halkier et al. [93] using the aug-cc-pVnZ (n = T,Q) basis sets. The core-correlation corrections were also included by calculating the energy difference between all electrons and the frozen-core approximation at the CCSD(T) level of theory using the aug-cc-pVTZ basis sets. Moreover, the scalar relativistic corrections were predicted using the Douglas-Kroll-Hess second-order scalar relativistic method [94,95] which was calculated by the difference between the CCSD(T)/aug-cc-pVTZ-DK and CCSD(T)/aug-cc-pVTZ results. The zero-point vibrational energies (ZPVE) were obtained with QCISD/cc-pVTZ. Single

point calculations with CCSD(T), QCISD(T) and QCISD(T,Full) were also performed employing the 6-311++G(3df,3pd), and in each case was used the optimized geometries and the ZPVE values obtained at QCISD/cc-pVTZ level.

The QTAIM and the NBO analysis were performed with the AIMALL [96] and NBO6 [97] programs, respectively. It will also use the Multiwfn program for the bond order analysis [98]. For these three analysis the PBE1PBE/cc-pVTZ method was used. The canonical Transition State Theory was used in the kinetic rate constant calculations which was carried out with the CCSD(T)/CBS//QCISD/cc-pVTZ method.

3. Results and Discussions

3.1. Structure Prediction

Fig. 1 presents the optimized structure of CH$_3$AsH$_2$ and CH$_2$AsH$_3$ with the QCISD, B3LYP, and M06 methods. Examining the methylarsine geometric parameters revealsed only slight differences in the bond lengths and angles between the methods. Regarding bond lengths, the errors were lower than 1% when compared to experimental values, with the exception of the carbon-arsenic bond. Based on the simulation results, BHandH and LC-wPBE predicted the lowest carbon-arsenic bond length values for methylarsine, ranging from 1.92 to 1.95 Å among the different basis sets, instead of the experimental value of 1.980 Å [14]. On the other hand, the B97D, BP86, and BPW91 functionals overestimated the carbon-arsenic bond length, leading to results close to 2.002 Å. Moreover, when a relativistic pseudo-potential basis set for the arsenic atom was analyzed, the changes in carbon-arsenic bond lengths are noted in the third decimal place; in contrast, employing Pople's basis sets resulted in an underestimation of the carbon-arsenic bond length among the DFT methods. Additional analysis of CH$_2$AsH$_3$ using the cc-pVQZ basis sets demonstrated that the carbon-arsenic bond length varied from 1.783 to 1.837 Å; LC-wPBE and B97D predicted the smallest and the largest results, respectively (see Table S1 in supporting material).

3.2. Methylarsine Vibrational Frequencies

Fig. 2 shows the methylarsine infrared spectrum predicted via the PBE1PBE functional. Methylarsine presents fifteen vibrational frequencies that are active in the infrared region, and all the vibration modes