Theoretical Study of the Relative Stabilities of Arsasilenes and Arsasilynes

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The unimolecular rearrangement of arsasilyne, XSi≡As (X = H, Li, Na, BeH, MgH, BH_2, AlH_2, CH_3, SiH_3, NH_2, PH_2, OH, SH, F, Cl), to arsasilene, Si=AsX, is considered using B3LYP and CCSD(T) calculations. The theoretical findings suggest that highly electronegative substitution occurs preferentially at silicon and, thus, strongly stabilizes triply bonded XSi≡As, with respect to doubly bonded Si=AsX, both from a thermodynamic and from a kinetic viewpoint.

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Although silicon lies just below carbon in the periodic table, its chemistry is surprisingly dissimilar. Much of the chemistry of carbon derives from its ability to readily form multiply bonded (and conjugated) compounds. On the other hand, it was not until 1981 that the first stable compounds with double bonds to silicon were synthesized and isolated.[1] Since then, doubly bonded silicon, such as Si=C,[2] Si=Pn (Pn = N, P, As)[3] and Si=Ch (Ch = O, S, Se),[4] has been well established and has been investigated extensively, both experimentally[5] and theoretically.[6] Nevertheless, while double bonds to silicon are apparently not prohibitively unstable, triple bonds containing silicon have mostly yet to be detected experimentally, except for the cases of HSi≡N[7] and HC≡SiX (X = F, Cl),[8] both of which were characterized spectroscopically. Indeed, for many years, the synthesis of stable compounds with triple bonds was a major challenge in silicon chemistry.[9]

In 1986, Märkl and Sejpka[10] reported the isolation of an arsaethyne, 2-(2,4,6-tri-*tert*-butylphenyl)-1-arsaethyne, which proved to be the first stable compound containing a C≡As triple bond. Since then, several arsaalkynes have been reported in the literature.[11−13] It is natural to consider whether organosilicon compounds with low-coordinated Si atoms and silicon−arsenic multiple bonds can exist. In fact, the first compound with a Si=As double bond, arsasilene, has recently been successfully synthesized and characterized.[14−16] From this point of view, it is important to determine if silicon is also capable of forming Si≡As triply bonded compounds. Despite several attempts, however, stable compounds containing a silicon−arsenic triple bond, arsasilyne, are still unknown. In view of the interest in isolating a Si≡As triple bond, it is inevitable to consider the possibility of stabilizing this moiety with some substituents. Experimental determinations of physical parameters for these generally short-lived, reactive silicon species are difficult to obtain and hence mostly nonexistent. Theory is therefore a potentially useful partner in the experimental investigation of the stability of arsasilyne. No quantum-chemical calculations for Si≡As triple-bond-containing molecules have yet been carried out, let alone a systematic theoretical study of substituent effects on the stabilities of arsasilyne species.

The purpose of the present work is therefore to explore the possible existence of a triply bonded

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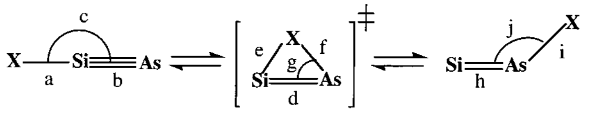
Table 1. Geometrical Parameters of Structures for Eq 1 at the B3LYP/6-311++G(d,p) Level of Theory (Distances in Å and Angles in Deg)



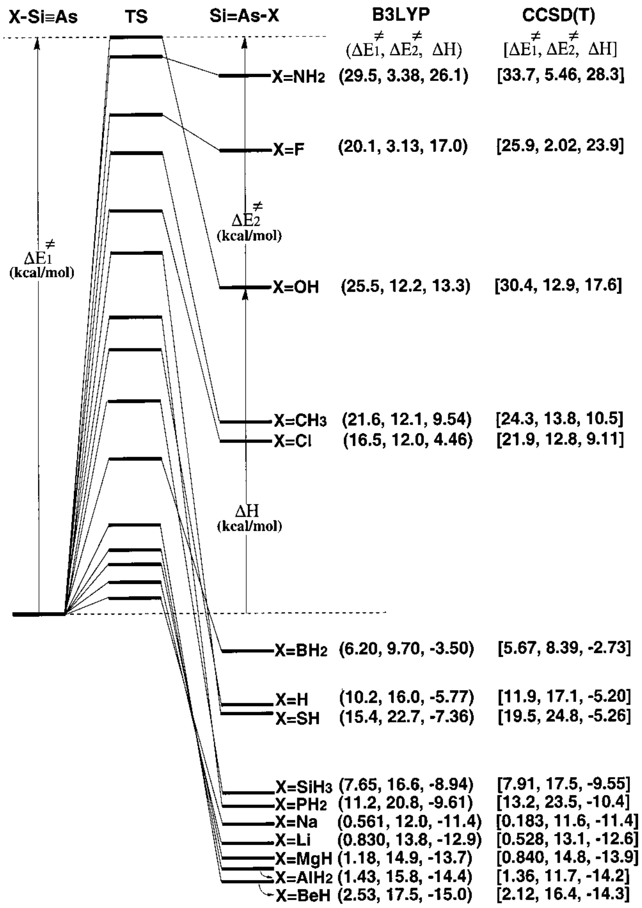
(1)

X	a	b[a]	c	d	e	f	g	h[a]	i	j
H	1.482	2.057 (2.82)	180.0	2.152	1.526	2.591	36.05	2.168 (1.68)	1.621	55.53
Li	2.407	2.087 (2.76)	180.0	2.095	2.395	4.112	25.42	2.135 (2.38)	2.429	73.48
Na	2.720	2.088 (2.69)	180.0	2.095	2.709	4.468	24.66	2.136 (2.34)	2.765	74.89
BeH	2.139	2.076 (2.80)	180.0	2.096	2.130	3.635	30.95	2.161 (2.04)	2.117	79.69
MgH	2.548	2.079 (2.76)	180.0	2.092	2.536	4.189	27.87	2.148 (2.17)	2.556	79.13
BH$_2$	1.969	2.079 (2.58)	180.0	2.131	2.030	2.676	48.33	2.160 (1.89)	1.998	107.1
AlH$_2$	2.436	2.078 (2.73)	180.0	2.096	2.423	3.973	30.81	2.181 (1.97)	2.426	75.44
CH$_3$	1.882	2.059 (2.79)	180.0	2.169	2.022	2.906	44.03	2.182 (1.91)	2.081	73.88
SiH$_3$	2.351	2.067 (2.71)	180.0	2.124	2.396	3.445	43.37	2.245 (1.75)	2.316	70.45
NH$_2$	1.699	2.065 (2.69)	179.9	2.215	2.007	2.979	42.34	2.223 (1.89)	1.886	109.8
PH$_2$	2.271	2.067 (2.54)	170.0	2.148	2.362	3.397	43.55	2.284 (1.34)	2.280	61.37
OH	1.639	2.062 (2.70)	179.3	2.307	1.721	2.854	37.08	2.233 (1.31)	2.092	52.18
SH	2.134	2.066 (2.79)	174.3	2.198	2.242	3.207	44.32	2.233 (1.38)	2.374	63.38
F	1.609	2.059 (2.71)	180.0	2.322	1.692	2.774	37.49	2.248 (1.24)	2.167	48.81
Cl	2.043	2.063 (2.35)	180.0	2.236	2.174	3.203	42.67	2.234 (1.59)	2.409	62.49

[a] Values in parentheses are bond orders based on the B3LYP/6-311++G(d,p) geometries.[22]

arsasilyne, given suitable substituents. For this purpose, we have used quantum-mechanical methods to investigate the influence of different substituted groups upon the relative stability of arsasilene (Si=AsX) and arsasilyne (XSi≡As) as well as on the transition states connecting them. Substituents X were selected from elements of the second and third rows of the periodic table such that the resulting XSiAs species were isovalent: i.e., X = H, Li, Na, BeH, MgH, BH$_2$, AlH$_2$, CH$_3$, SiH$_3$, NH$_2$, PH$_2$, OH, SH, F, Cl (see eq 1 in Table 1). Results are reported for the structures of these systems and for their stabilities with respect to unimolecular rearrangement. All of the above species are presently unknown but appear to offer good prospects for experimental realization. It is believed that extensive studies of silicon−arsenic multiply bonded compounds should soon be forthcoming and open up new areas soon.

Scheme 1



The geometries and energetics of the stationary points on the potential energy surface of eq 1 have been calculated using density functional theory (DFT), i.e., B3LYP methods,[17] in conjunction with the 6-311++G(d,p) basis set.[18] All the stationary points have been positively identified as equilibrium structures (the number of imaginary frequency (NIMAG = 0)) or transition states (NIMAG = 1). Additionally, the vibrational zero-point energy (ZPE) corrections determined at the B3LYP/6-311++G(d,p) level are also included: i.e., B3LYP/6-311++G(d,p) + ZPE (B3LYP/6-311++G(d,p)) (hereafter designated B3LYP/6-311++G(d,p)). For better energetics, single-point calculations with B3LYP/6-311++G(d,p) geometries were carried out at a higher level of theory: coupled cluster singles and doubles including a perturbational estimate of the triples (CCSD(T)).[19] Unless otherwise noted, the relative energies given in the text and in Scheme 1 are those determined at CCSD(T)/6-311++G(3df,3pd)//B3LYP/6-311++G(d,p) + ZPE (B3LYP/6-311++G(d,p)) (hereafter designed CCSD(T)).[20] All calculations were carried out using the Gaussian 98 series of programs.[21]

Selected geometrical parameters of XSi≡As, Si=AsX, and the transition state for the reaction XSi≡As → Si=AsX (i.e., eq 1) are given in Table 1. The calculated

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vibrational frequencies, rotational constants, dipole moments, and net atomic charges are given in Table 2 (see the Supporting Information). Also, the potential energy profiles at the B3LYP and CCSD(T) levels are summarized in Scheme 1. The major conclusions that can be drawn from these tables and Scheme 1 are as follows.

First, the B3LYP Hessian calculations show that all of the $\mathrm{XSi{\equiv}As}$ and $\mathrm{Si{=}AsX}$ isomers are local minima (see Table 1). It appears that electron-withdrawing or π-donating substitution tends to strengthen the $\mathrm{Si{\equiv}As}$ bond in the $\mathrm{XSi{\equiv}As}$ species. Conversely, electropositive or π-accepting substitution seems to weaken the $\mathrm{Si{\equiv}As}$ bond. A possible explanation for this is the fact that electronegative substitution induces a large positive charge on the Si atom and a small increase in electron density on the As atom (see Table 2). As a result, the more electronegative the substituent X attached to silicon, the more positive the charge at silicon, the higher the degree of bond ionicity, and the shorter the $\mathrm{Si{\equiv}As}$ triple bond becomes. On the other hand, the effect of substituents on the $\mathrm{Si{=}As}$ bond in the $\mathrm{Si{=}AsX}$ species is just the opposite. Here, electronegative substitution results in a longer $\mathrm{Si{=}As}$ bond, while electropositive substitution has the opposite effect.

Second, the results for the geometries of the XSiAs species are one of the most interesting results of the present study, since very little is known about their structures. As Table 1 shows, our B3LYP calculations predict that the triply bonded $\mathrm{XSi{\equiv}As}$ species are linear, while the doubly bonded $\mathrm{Si{=}AsX}$ species exist as bent molecules. In addition, our DFT results suggest that linear $\mathrm{Si{=}AsX}$ isomers are not stable structures. They have two imaginary vibrational frequencies corresponding to a bending mode, leading to the bent isomer. Furthermore, bond orders for those XSiAs species have also been calculated by using the B3LYP level of theory,[22] which are collected in Table 1. Basically, the covalent bond orders in the $\mathrm{XSi{\equiv}As}$ and $\mathrm{Si{=}AsX}$ molecules follow the expectations based on chemical intuition: that is to say, the covalent bond orders of the bonds between the silicon and arsenic atoms are close to 3 and 2, respectively.

Third, the transition state geometries for the unimolecular isomerizations of XSiAs are already given in Table 1. All these transition states possess one imaginary frequency and are true first-order saddle points. In these transition states the substituent X is positioned under the Si−As bond, forming a three-membered ring. Also, it should be noted that Si−X bonds broken in the transition structures are 3.0% (HSiAs-TS), 0.50% (LiSiAs-TS), 0.40% (NaSiAs-TS), 0.42% (HBeSiAs-TS), 0.47% (HMgSiAs-TS), 3.1% ($\mathrm{H_2BSiAs}$-TS), 0.53% ($\mathrm{H_2AlSiAs}$-TS), 1.9% ($\mathrm{H_3SiSiAs}$-TS), 7.4% ($\mathrm{H_3CSiAs}$-TS), 4.9% ($\mathrm{H_2NSiAs}$-TS), 4.0% ($\mathrm{H_2PSiAs}$-TS), 5.0% (HOSiAs-TS), 11% (HSSiAs-TS), 5.2% (FSiAs-TS), and 6.4% (ClSiAs-TS) longer than those in the corresponding $\mathrm{XSi{\equiv}As}$ species. According to Hammond's postulate,[23] this indicates that transition structures with electropositive substituents (such as Li, Na, BeH, MgH, $\mathrm{BH_2}$, $\mathrm{AlH_2}$, and $\mathrm{SiH_3}$) take on a more reactant-like character than those of the other XSiAs species with electronegative substituents (e.g., $\mathrm{CH_3}$, $\mathrm{NH_2}$, $\mathrm{PH_2}$, OH, SH, F, and Cl). Therefore, the barriers should be encountered earlier in the unimolecular rearrangement of the former as compared to the latter. This prediction is confirmed by our computational results. As one can see in Scheme 1, the potential energy barriers ($\Delta E_1^{\ddagger}$) for the $\mathrm{XSi{\equiv}As}$ species with electropositive substituents are apparently much lower than those for the $\mathrm{XSi{\equiv}As}$ molecules with electronegative substituents. In other words, this strongly implies that the $\mathrm{XSi{\equiv}As}$ species with electropositive substituents are considerably less stable in a kinetic sense than those with electronegative substituents.

Fourth, as can be seen in Scheme 1, not only the barrier height but also the enthalpy correlates with the electronegativity of the substituent X. In other words, the more electropositive the substituent X, the lower the activation barrier ($\Delta E_1^{\ddagger}$) for the isomerization reaction $\mathrm{XSi{\equiv}As} \rightarrow \mathrm{Si{=}AsX}$ (from left to right in eq 1), but also the larger the enthalpy (ΔH) for this unimolecular rearrangement and the lower the heat ($\Delta E_2^{\ddagger}$) of the reverse reaction (right to left in eq 1). Again, our computational results follow the Hammond postulate: an earlier transition state leads to a smaller barrier and a more exothermic reaction. Accordingly, for the case of electropositive substitution, the large energy difference favoring $\mathrm{Si{=}AsX}$ over $\mathrm{XSi{\equiv}As}$ indicates that silicon is more reluctant to form triply bonded than doubly bonded compounds with arsenic. Besides this, our computational results suggest that the relative stabilities of doubly bonded ($\mathrm{Si{=}AsX}$) and triply bonded ($\mathrm{XSi{\equiv}As}$) species can be dramatically reversed when substituents are replaced by electronegative groups. Namely, the highly electronegative substitution occurs preferentially at silicon and greatly stabilizes the $\mathrm{XSi{\equiv}As}$ species relative to the $\mathrm{Si{=}AsX}$ species. For instance, our CCSD(T) calculations predict that the energies of the $\mathrm{Si{=}AsX}$ molecules are above the energies of the corresponding $\mathrm{XSi{\equiv}As}$ molecules by 28, 18, 10, 9.1, and 24 kcal/mol for $\mathrm{X = NH_2}$, OH, $\mathrm{CH_3}$, Cl, F, respectively. In contrast, the energies of the $\mathrm{Si{=}AsX}$ species are lower than those of the corresponding $\mathrm{XSi{\equiv}As}$ compounds by 2.7, 5.2, 9.5, 13, and 14 kcal/mol for $\mathrm{X = BH_2}$, H, $\mathrm{SiH_3}$, Li, and BeH, respectively. Moreover, the barriers ($\Delta E_2^{\ddagger}$) of the electronegative substituted $\mathrm{Si{=}AsX}$ for the reverse process (i.e., right to left in eq 1) are quite small (about 2.0−13 kcal/mol; see Scheme 1), compared to those of the electropositive substituted $\mathrm{Si{=}AsX}$ (at least $>$8.4 kcal/mol). Obviously, this makes electronegative substitution more facile in the formation of $\mathrm{XSi{\equiv}As}$ triply bonded compounds.

Fifth, the thermodynamic stabilizing effect of electronegative substituents may perhaps be due in part to the strength of Si−X vs As−X bonds. In other words, a strong Si−X bond and a weak As−X bond can overturn

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the intrinsic preference of Si═AsX over XSi≡As. For example, some available experimental bond dissociation energies (in kcal/mol) are as follows:[24] Si−F (132), As−F (98.0); Si−O (191), As−O (115); Si−N (117), As−N (112); Si−Cl (97.0), As−Cl (107); Si−P (87.0), As−P (104). Therefore, it appears that the change in Si−X and As−X bonding is parallel to the order of relative stabilities of XSi≡As and Si═AsX, as long as bond energy−bond length relationships are valid.

In summary, this work represents an attempt to apply a simple model to understand electronic effects on the relative stability of the arsasilene and arsasilyne species. The present study predicts that the arsasilyne XSi≡As itself lies at the minimum of the potential energy surface and can be greatly stabilized in both a kinetic and a thermodynamic sense, with the proper choice of substituents. Also, on the basis of the present theoretical results, it is suggested that second-row elements stabilize Si≡As triple bonds more effectively than the corresponding third-row elements. Since the electronegativity of the second-row substituents is larger than that of their third-row counterparts, this effect appears to play a prominent role in the difference in stabilization between the two rows, and in determining the barrier heights as well as the reaction enthalpy for the unimolecular rearrangement. In particular, highly electronegative substituents (such as X = F, NH_2, OH) can preferentially stabilize XSi≡As, with respect to Si═AsX, from both the thermodynamic and kinetic points of view. Dimerization or the formation of even higher aggregates may be possible, but the detection of the XSi≡As species as a monomer should be achieved in the low-pressure gas phase (e.g. as low as 10^{-4} Torr) or in the low-temperature matrix. In other words, it is predicted that the XSi≡As species with highly electronegative substitution should have a lifetime long enough for them to be observed experimentally.

It is hoped that our study will stimulate further research in this area.

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Supporting Information Available: Table 2, giving calculated vibrational frequencies, rotational constants, dipole moments, and net atomic charges. This material is available free of charge via the Internet at http://pubs.acs.org.

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