

# Thermochemical considerations and bond enthalpy ratios involving triatomic 16-valence electron neutrals and ions and some isoelectronically related pentaatomics<sup>☆</sup>

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## Abstract

Following thermochemical studies and the accompanying analysis in the calorimetric literature, in earlier computational and conceptual studies we investigated the systematics of the mean bond enthalpy ratio  $\langle D_m^\circ(XY_2) \rangle / D_m^\circ(XY)$  for 16-valence electron neutral and ionic triatomic species. For neutral species wherein X is a group 14 element and Y is from group 16, the ratio was ca. 0.8 rising to ca. 0.9 for the corresponding anions with X from group 13, and falling to ca. 0.7 for the cations with X from group 15. Good agreement between theory and experiment was found where admittedly the majority of the data for the latter is for the neutral species. In the current study at the G2 computational level (and G3 for selected systems), the related asymmetric valence isoelectronic triatomic species YXZ are discussed and this pattern computationally preserved. The results are in concurrence with the one experimentally available datum for comparison, namely from the literature measured value for the enthalpy of formation of OCS. Other surprises and systematics are discussed as well for what otherwise might have been superficially considered to be simple species, for these and related pentaatomic species of the type HXYXH.

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## 1. Introduction

Following thermochemical studies and the accompanying analysis in the calorimetric literature [1], in earlier computational and conceptual studies we investigated the systematics [2,3] of the mean bond enthalpy ratio  $\langle D_m^\circ(XY_2) \rangle / D_m^\circ(XY)$  for 16-valence electron neutral and ionic triatomic species. Again following the literature, we chose the Y atoms from the group 16 elements (the lighter chalcogens O, S, and Se) and because the charges were limited to 0, +1, and -1, the X atoms were

chosen from group 14, 15, and 13, respectively (C, Si, Ge; N, P, As; B, Al, Ga).

Despite the seeming simplicity of these species in terms of the number of atoms and electrons, the set of valence isoelectronic (equivalently called isovalent) compounds, the asymmetric triatomic 16-valence electron species, [YXZ], is surprisingly poorly represented in the chemical literature. (For this article, each chemical formula is explicitly written to denote the connectivity.) For example, while the nitronium cation, [ONO]<sup>+</sup>, is well known to the synthetic, reaction and thermochemical communities and its disulfur analog [SNS]<sup>+</sup> is ever more available through a convenient synthesis and is thus now better understood by them as well [4], there is seemingly no analogous information nor any synthetic pathway for the corresponding mixed species [ONS]<sup>+</sup>. While anionic borates have long been known in both the condensed and gas phase, and diverse sulfur analogs have also been characterized, such species containing both oxygen and sulfur are seemingly limited to the sodium salt of (B<sub>5</sub>O<sub>8</sub>S)<sup>3-</sup>

<sup>☆</sup> In memory of Sharon Lias, colleague and friend.

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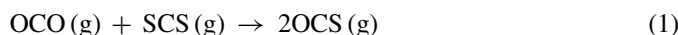
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[5] which, with its spirocyclic structure, offers no insight into the simpler triatomic [OBS]<sup>−</sup>.

Indeed, following our own scientific interests and those of Sharon Lias, we return now to gas phase species and their energetics. And here we find that the only such mixed species, neutral or ionic, for which enthalpy of formation data [6] is available is carbonyl sulfide, OCS,  $\Delta_f H^\circ(\text{g}) = -142.0 \pm 0.3$  kJ/mol. All unreferenced enthalpies of formation will be assumed taken from this source [6].

The relatively few theoretical studies on the [YXZ]<sup>q</sup> species include evaluations of the lithium cation and proton affinities of the anions with X = B<sup>−</sup>, Al<sup>−</sup> and Y = O, S and the proton affinities of the neutrals with X = C, Si [7–9]. Additional molecular properties, such as spectroscopic constants and isomeric structures and stabilities, of these and other sulfur-containing species (e.g., [ONS]<sup>+</sup> [10–12] and SCSe [13]) have also been investigated. The atomization energies of YCZ molecules [14] and the IR spectra of YGeZ molecules [15] have been calculated. Reaction pathways have been computed for the production of OCS or OCSe from the addition of O atoms to SCSe, SCS, and SeCS [16].

Consider the formal oxygen-sulfur exchange reaction in Eq. (1).



This reaction is exothermic by but  $7.2 \pm 1.0$  kJ/mol (the data for CO<sub>2</sub> is from Ref. [17]). That the reaction is rather close to being thermoneutral seems quite sensible in terms of bond additivity, i.e., it is a shuffle of localized double bonds found in a cumulenenic, not conjugated, way. Then it is seen that the oxygen-methylene exchange reaction (Eq. (2)) involving the likewise isoelectronic H<sub>2</sub>CCCH<sub>2</sub>, H<sub>2</sub>CCO, and OCO is found to be endothermic by  $108.0 \pm 2.6$  kJ/mol, using archival enthalpies of formation for all three species. (Perhaps the disparate names of these three species (allene, ketene, and carbon dioxide) correctly betray the very disparate chemistry and thermochemistry for them.)



The first part of the current article addresses the question: how close to thermoneutral is the following exchange reaction related to reaction (1).



Following our earlier studies [2,3] YXY, ZXZ, and YXZ are 16-valence electron containing triatomic molecules or isoelectronically related singly charged ions. As such, X is limited to the group 14 C and its congeners, Si and Ge; group 13 anions, B<sup>−</sup> and thereby Al<sup>−</sup> and Ga<sup>−</sup>; group 15 cations, N<sup>+</sup> and thereby P<sup>+</sup> and As<sup>+</sup>. Y and Z are in all cases the group 16 O and the related S and Se. Lacking experimental data for almost all cases wherein Y ≠ Z, we present only the results from our quantum chemical findings for all species discussed herein.

The second and third parts of the current article discuss the thermochemistry of reactions related to reaction (2) wherein Y and/or Z are more complicated than “merely” chalcogens. The

second part discusses our quantum chemical findings for only a small number of cases compared to what may be plausibly considered. (In principle, for all of the aforementioned central atoms X, the outer species Y, and thus Z, could be taken from NH, PH, and AsH; CH<sub>2</sub>, SiH<sub>2</sub>, and GeH<sub>2</sub>, as well as their derivatives wherein any and all H's could be replaced by other univalent groups.) The third part discusses some of the comparatively few examples from the experimental literature. (Even here, there are some restrictions. The central atom will always be seen to be C. Estimates will still be needed to be made but these are well preceded from the physical organic chemistry literature of substituted species.)

The fourth part of our paper looks beyond the energetics of reaction (3) to probe the constancy of the bond enthalpy ratio

$$\frac{[D_m^\circ(\text{YXZ} \rightarrow \text{Y} + \text{X} + \text{Z})]}{[D_m^\circ(\text{XY} \rightarrow \text{X} + \text{Y}) + D_m^\circ(\text{XZ} \rightarrow \text{X} + \text{Z})]} \quad (4)$$

When Y = Z, this reduces to an earlier literature expression, first written by O'Hare and Curtiss [1] for a comparatively small number of neutral triatomic molecules and then studied by us for a significantly larger set of isoelectronic neutral [2] and ionic [3] triatomic molecules. Following our earlier analysis, we will consider isoelectronic and valence isoelectronic dissociation processes. That is, the central atom X will be assumed to always have 4 valence electrons. As such, where X is a group 14 element it will be neutral as befits the dissociation of a neutral molecule. Where X is from group 13 it will be have a negative charge even though the central B, Al, and Ga atoms are less electronegative than the outer chalcogen atoms and so B<sup>−</sup>, Al<sup>−</sup>, and Ga<sup>−</sup> are perhaps unexpected dissociation products—and perhaps, even more so, unexpectedly written for the parent triatomic itself. Relatedly, where X is from group 15, it will be given a positive charge even though sometimes (e.g., X = N), the ionization potential is higher than that of the attached atoms even if the electronegativity is lower. (A similar issue arises in discussions of basicity and proton affinities, e.g., of amines. A positive charge is not uncommonly put on the nitrogen in textbook drawings of ammonium ions even though quantum chemical calculations show it to be negative [18,19]). Relatedly, the reaction connecting amines – and indeed most bases – and their “onium” ions is given by Eq. (5), even though the thermodynamically preferred dissociation products are B<sup>+</sup> + H [20–24].



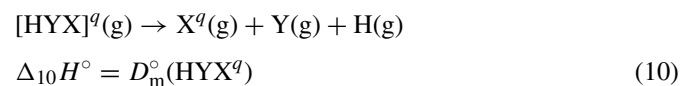
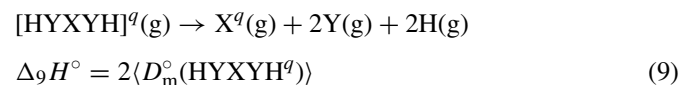
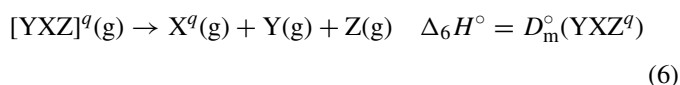
We also consider some pentaatomic species wherein Y and Z are now NH, PH, and AsH, where the dissociation process involves formation of these species explicitly as diatomics.

However, for the current study as for our earlier ones, we do not consider the well-known ions N<sub>3</sub><sup>−</sup>, NCO<sup>−</sup>, and NCS<sup>−</sup> (azide, cyanate, and thiocyanate) or any of their isoelectronic and valence isoelectronic analogs. The corresponding dissociations involve formation of N<sup>−</sup> and its analogs, a process conceptually complicated by the fact that N<sup>−</sup> is unbound with regards to loss of an electron [25].

## 2. Computational details

Structural parameters and relative stabilities of the 10- and 16-valence electron species HYX, [HYX]<sup>+</sup> and YXZ, [YXZ]<sup>±</sup>, HYXYH, [HYXYH]<sup>+</sup>, respectively, were determined with the composite G2 method [26,27]. As in our earlier work [2,3] on the related species XY, [XY]<sup>±</sup>, YXY, and [YXY]<sup>±</sup>, the G2 method was modified by evaluating equilibrium geometries and vibrational frequencies (scaled by 0.9646 [28]) at the MP2(full)/6-311G(d) ([YXZ]<sup>q</sup>) or MP2(full)/6-31G(d) ([HYXYH]<sup>q</sup>) level of theory. In order to assess the effect of diffuse functions on the geometries of the anions, we also evaluated MP2(full)/6-311+G(d) equilibrium geometries for [YXZ]<sup>-</sup> and [YXY]<sup>-</sup>. In addition, G3 calculations [29] were carried out for all of the above systems containing first- or second-row atoms for which the G3Large basis set [29] is stored internally in the Gaussian 03 program package [30]. The G3 data were obtained to corroborate the G2 data for some of the systems for which the greatest discrepancies in disproportionation reaction enthalpies and/or bond dissociation enthalpy ratios were observed. The vibrational analysis was used to characterize all structures as energy minima or saddle points on the corresponding electronic hypersurfaces.

The total bond dissociation enthalpies are defined as the changes in enthalpy at 298 K and 1.0 atm for reactions (6)–(10), in which all reactants and products are in their ground states. The molecular and atomic enthalpies were computed as the sum of the total energy, zero-point vibrational energy and enthalpy temperature corrections. For the asymmetric triatomic 16-valence electron species Y, Z = O, S, Se with X = B, Al, Ga; C, Si, Ge; N, P, As and  $q = -1, 0, +1$ . For the pentaatomic species Y = N, P, As with X = C, Si, Ge; N, P, As and  $q = 0, +1$ .



Linear and bent arrangements were examined for the triatomics [YXZ]<sup>q</sup> and [HYX]<sup>q</sup>, and the eight arrangements illustrated in Fig. 1, designated **a–h**, were examined for the pentaatomics [HYXYH]<sup>q</sup>. In addition to the completely linear  $D_{\infty h}$  structure (**a**), acyclic twisted  $C_2$  (**b**), cyclic twisted  $C_2$  (**c**), cyclic orthogonal  $C_s$  (**d**), and planar  $C_{2h}$  (**e**),  $C_s$  (**f**), and  $C_{2v}$  (**g** and **h**) structures were considered. Indeed the simplest localized Lewis structure (atoms with no formal charges and do not worry about an octet around each heavy atom) for HYX and HYXYH has a

bent arrangement around Y, i.e., H–Y = X and H–Y = X = Y–H, respectively.

An NBO [31] analysis of the Hartree-Fock molecular orbitals was performed for the [YXZ]<sup>q</sup>, [YXY]<sup>q</sup> and [ZXZ]<sup>q</sup> systems. The NBO analysis [32–36] considers deviations of the molecule from the strictly localized Lewis structure. For these triatomic species, the Lewis NBOs describe about 99% of the total electron density. The analysis also allows one to evaluate changes in hybridization and polarization on bond formation. Since there were few consistent patterns in the bond length and bond angle changes for the [HYXYH]<sup>q</sup> systems as a function of X and Y, no NBO analysis was done for those systems.

## 3. Results and analysis of results

### 3.1. Exchange reactions

G2 and G3 bond dissociation enthalpies for [YXZ]<sup>q</sup> ( $q = -1, 0, +1$ ) are given in Table 1. For convenience, also included in the table are the G2 bond dissociation enthalpies from references [2] and [3] for those YXY and ZXZ neutral and ionic systems for which we have obtained G3 data. The G2 values were calculated with the atomic energies of As<sup>+</sup>, Ge, and Se stabilized by first-order spin–orbit corrections from reference [37]. As in our earlier work on the symmetric species such as OCO, we estimate that the correction term for Ga<sup>-</sup> is indistinguishable from zero [3]. This estimate is based on the trend in <sup>3</sup>P<sub>0</sub>, <sup>3</sup>P<sub>1</sub>, and <sup>3</sup>P<sub>2</sub> energy levels found in Moore's tables for the isoelectronic series Br<sup>3+</sup>, Se<sup>2+</sup>, As<sup>+</sup>, and Ge and the drop in the spin–orbit correction term for Ge with respect to that of As<sup>+</sup> [37,38]. The bond dissociation enthalpies and bond lengths (Table S1) reported for [YXZ]<sup>q</sup> are limited to those for the linear structure since, similarly to the [YXY]<sup>q</sup>/[ZXZ]<sup>q</sup> ( $q = -1, 0, +1$ ) species, bent or cyclic structures are considerably less stable (this work and references [2,3,39]).

The largest discrepancy between the G2 and G3 data is 19 kJ/mol (Table 1), and the mean absolute deviation between the two sets of data is  $6 \pm 4$  kJ/mol. There is no uniform trend when comparing the G2 and G3 enthalpies; G2 values are both overestimated and underestimated with respect to the corresponding G3 value. In contrast, as was reported previously [2,3] for the neutral and ionic triatomics with identical terminal atoms, G2(MP2) [40] bond dissociation enthalpies are uniformly too large compared to the G2 values (data not shown). The overestimations range from 5 to 20 kJ/mol.

The only set of [YXZ]<sup>q</sup>, [XY]<sup>q</sup>, and [XZ]<sup>q</sup> species for which experimental thermochemical data are available is OCS, CO, and CS. The enthalpy of formation of OCS at 298 K is  $-142.1$  kJ/mol ( $-142.2$  at 0 K). From the  $\Delta_f H^\circ$ s of atomic C, O, and S of 716.7, 249.2, and 278.8 kJ/mol, respectively, the atomization enthalpy of OCS is 1387 kJ/mol, in excellent agreement with the G2 and G3 calculated enthalpies of 1392 kJ/mol (Table 1).

The [YGaZ]<sup>-</sup> system is the one system for which unexpected results are found in Table 1. First, the bond dissociation enthalpy of [OGaS]<sup>-</sup> does not lie between that of [OGaO]<sup>-</sup> and [SGaS]<sup>-</sup>. Second, these are the only systems for which

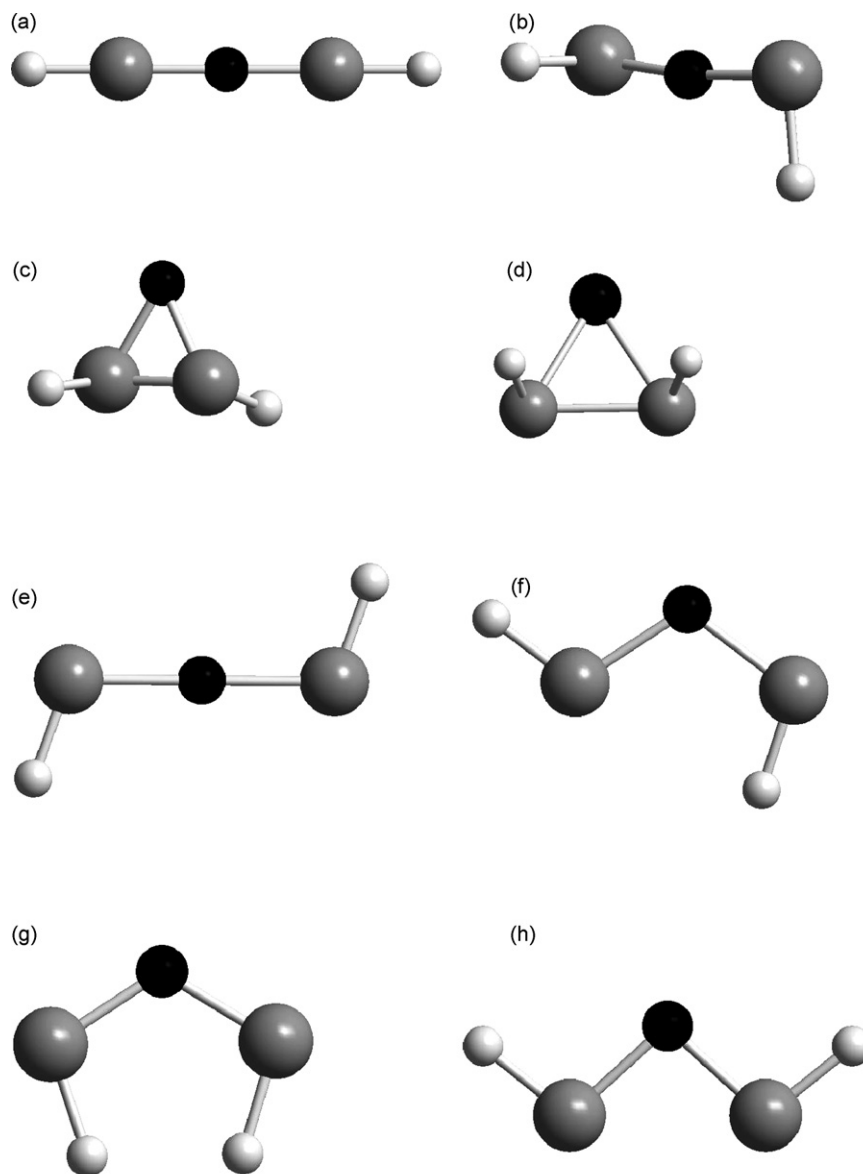


Fig. 1. Diagrams of the eight geometrical configurations investigated for the HXYXH systems. X: black, Y: gray, H: white. **a:** Linear  $D_{\infty h}$  configuration; **b:** acyclic twisted  $C_2$  configuration; **c:** cyclic twisted  $C_2$  configuration; **d:** cyclic orthogonal  $C_s$  configuration; **e:**  $C_{2h}$  configuration; **f:** planar  $C_s$  configuration; **g:**  $C_{2v}$  configuration; **h:** W-shaped  $C_{2v}$  configuration.

the bond dissociation enthalpies of the asymmetric triatomics do not decrease as Y and Z go down group 16. The trend for these systems is  $[\text{OGaS}]^- > [\text{SGaSe}]^- > [\text{OGaSe}]^-$ . The trends for the related  $[\text{YGaY}]^-$  and  $[\text{GaY}]^-$  are similarly anomalous,  $[\text{SGaS}]^- > [\text{OGaO}]^- > [\text{SeGaSe}]^-$  and  $[\text{GaS}]^- > [\text{GaSe}]^- > [\text{GaO}]^-$ , respectively [3].

Table 2 presents the reaction enthalpies for the exchange reactions given in Eq. (3). For the limited data available, despite the discrepancies in the G2 and G3 bond dissociation enthalpies, there is little discrepancy in the G2 and G3 exchange reaction enthalpies. The G2 enthalpies required to break the first XY or XZ bond in a  $[\text{YXZ}]^q$ ,  $[\text{YXY}]^q$  or  $[\text{ZXZ}]^q$  triatomic are listed in Table 3. The differences in the enthalpies  $\Delta\text{BE}$  required to break the XY bond in  $[\text{YXZ}]^q$  and  $[\text{YXY}]^q$  (Eq. (11)) and the XZ bond in  $[\text{YXZ}]^q$  and  $[\text{ZXZ}]^q$  (Eq. (12)) are also tabulated. Note that

the spin-orbit and higher-level (HLC) corrections cancel in the exchange reaction enthalpies and the bond enthalpy differences  $\Delta\text{BE}$ .

$$\Delta\text{BE} = G2([\text{YXZ}]^q \rightarrow [\text{XZ}]^q + \text{Y}) - G2([\text{YXY}]^q \rightarrow [\text{XY}]^q + \text{Y}) \quad (11)$$

$$\Delta\text{BE} = G2([\text{YXZ}]^q \rightarrow [\text{XY}]^q + \text{Z}) - G2([\text{ZXZ}]^q \rightarrow [\text{XZ}]^q + \text{Z}) \quad (12)$$

The disproportionation reactions are essentially thermoneutral for all of the neutral triatomics (Table 2). This observation also holds when Y = S and Z = Se, regardless of the nature of X. In contrast, when Y = O and Z = S, Se, the exchange reac-

Table 1  
Calculated vs. experimental bond dissociation enthalpies,  $D_m^\circ$  <sup>a,b</sup>

Species	$D_m^\circ$ G2 (298 K)	$D_m^\circ$ G3 (298 K)	$D_m^\circ$ (expt) <sup>c</sup>
[OBS] <sup>-</sup>	1578	1581	
[OBSe] <sup>-</sup>	1504		
[SBSe] <sup>-</sup>	1276		
[OBO] <sup>-</sup>	1764	1759	1532, 1650
[SBS] <sup>-</sup>	1358	1368	
[BO] <sup>-</sup>	1041	1035	861
[BS] <sup>-</sup>	768	769	
[OAlS] <sup>-</sup>	1179	1185	
[OAlSe] <sup>-</sup>	1126		
[SAIS] <sup>-</sup>	1044		
[OAlO] <sup>-</sup>	1258	1261	1366
[SAIS] <sup>-</sup>	1098	1106	
[AlO] <sup>-</sup>	725	721	815
[AlS] <sup>-</sup>	637	639	
[OGaS] <sup>-</sup>	970		
[OGaSe] <sup>-</sup>	928		
[SGaSe] <sup>-</sup>	964		
OCS	1392	1392	1387 <sup>d</sup>
OCSe	1295		
SCSe	1061		
OCO	1620	1612	1608
SCS	1160	1166	1156
CO	1088	1077	1076
CS	720	717	709
OSiS	1083	1086	
OSiSe	1016		
SSiSe	872		
OSiO	1226	1228	1228
SSiS	938	945	966
SiO	798	798	792
SiS	612	614	617
OGeS	891		
OGeSe	836		
SGeSe	761		
[ONS] <sup>+</sup>	1421	1414	
[ONSe] <sup>+</sup>	1359		
[SNS] <sup>+</sup>	1329		
[ONO] <sup>+</sup>	1420	1408	1400
[SNS] <sup>+</sup>	1396	1397	1357
[NO] <sup>+</sup>	1146	1127	1150
[NS] <sup>+</sup>	1024	1016	916 <sup>e</sup>
[OPS] <sup>+</sup>	1012	1006	
[OPSe] <sup>+</sup>	969		
[SPSe] <sup>+</sup>	878		
[OPO] <sup>+</sup>	1076	1065	1094
[SPS] <sup>+</sup>	926	925	
[PO] <sup>+</sup>	799	789	800
[PS] <sup>+</sup>	682	676	
[OAsS] <sup>+</sup>	774		
[OAsSe] <sup>+</sup>	744		
[SAsSe] <sup>+</sup>	716		

<sup>a</sup> Enthalpies in kJ mol<sup>-1</sup>. Total bond dissociation enthalpies for diatomic and triatomic systems. See Eqs. (6)–(8) in the text for definitions.

<sup>b</sup> G2 values include spin–orbit corrections for Ge and Se from reference [37].

<sup>c</sup> Neutrals: reference [1]. Cations and anions: reference [23].

<sup>d</sup> Reference [6].

<sup>e</sup> Reference [94].

tion enthalpies are as large in magnitude as 50 kJ/mol. Although the computed enthalpies associated with the exchange reactions involving [OXZ]<sup>±</sup> range from only 1–5% of the bond dissociation enthalpies of these ions, there is a significant difference

Table 2  
Disproportionation reaction enthalpies<sup>a</sup>

Reaction	G2 (298 K)	G3 (298 K)	Expt. <sup>b</sup>
[OBO] <sup>-</sup> + [SBS] <sup>-</sup> → 2[OBS] <sup>-</sup>	-34	-36	
[OBO] <sup>-</sup> + [SeBSe] <sup>-</sup> → 2[OBSe] <sup>-</sup>	-53		
[SBS] <sup>-</sup> + [SeBSe] <sup>-</sup> → 2[SBSe] <sup>-</sup>	-2		
[OAlO] <sup>-</sup> + [SAIS] <sup>-</sup> → 2[OAlS] <sup>-</sup>	-2	-2	
[OAlO] <sup>-</sup> + [SeAlSe] <sup>-</sup> → 2[OAlSe] <sup>-</sup>	-5		
[SAIS] <sup>-</sup> + [SeAlSe] <sup>-</sup> → 2[SAlSe] <sup>-</sup>	-1		
[OGaO] <sup>-</sup> + [SGaS] <sup>-</sup> → 2[OGaS] <sup>-</sup>	50		
[OGaO] <sup>-</sup> + [SeGaSe] <sup>-</sup> → 2[OGaSe] <sup>-</sup>	44		
[SGaS] <sup>-</sup> + [SeGaSe] <sup>-</sup> → 2[SGaSe] <sup>-</sup>	0		
OCO + SCS → 2OCSe	-3	-5	-2
OCO + SeCSe → 2OCSe	-10		
SCS + SeCSe → 2SCSe	-1		
OSiO + SSiS → 2OSiS	-1	2	
OSiO + SeSiSe → 2OSiSe	1		
SSiS + SeSiSe → 2SSiSe	0		
OGeO + SGeS → 2OGeS	1		
OGeO + SeGeSe → 2OGeSe	0		
SGeS + SeGeSe → 2SGeSe	0		
[ONO] <sup>+</sup> + [SNS] <sup>+</sup> → 2[ONS] <sup>+</sup>	-25	-24	
[ONO] <sup>+</sup> + [SeNSe] <sup>+</sup> → 2[ONSe] <sup>+</sup>	-39		
[SNS] <sup>+</sup> + [SeNSe] <sup>+</sup> → 2[SNSe] <sup>+</sup>	-5		
[OPO] <sup>+</sup> + [SPS] <sup>+</sup> → 2[OPS] <sup>+</sup>	-22	-23	
[OPO] <sup>+</sup> + [SePSe] <sup>+</sup> → 2[OPSe] <sup>+</sup>	-33		
[SPS] <sup>+</sup> + [SePSe] <sup>+</sup> → 2[SPSe] <sup>+</sup>	-2		
[OAsO] <sup>+</sup> + [SAsS] <sup>+</sup> → 2[OAsS] <sup>+</sup>	-20		
[OAsO] <sup>+</sup> + [SeAsSe] <sup>+</sup> → 2[OAsSe] <sup>+</sup>	-32		
[SAsS] <sup>+</sup> + [SeAsSe] <sup>+</sup> → 2[SAsSe] <sup>+</sup>	-1		

<sup>a</sup> Reaction enthalpies in kJ/mol.

<sup>b</sup> Reference [6].

in the results for the oxygen-containing ions from those of the remaining species.

As one might expect for the thermoneutral exchange reactions, the data in Table 3 demonstrate that when Y = S and Z = Se the strength of the X–S bond is similar in [SXSe]<sup>q</sup> and [SXS]<sup>q</sup>, as is the strength of the X–Se bond in [SXSe]<sup>q</sup> and [SeXSe]<sup>q</sup>. Generally the bond strengths differ by 10 kJ/mol or less and the  $\Delta$ BE values are opposite in sign. However, for each X other than Ga<sup>-</sup> and Al<sup>-</sup>, when Y = O the X–O bond in [OXSe]<sup>q</sup> is considerably stronger than the X–O bond in [OXO]<sup>q</sup>. The deviation in the two bond enthalpies ranges from 35 to 165 kJ/mol, with the larger values associated with an X from the 2nd row (i.e., Li–Ne). Compared to [SXS]<sup>q</sup> or [SeXSe]<sup>q</sup>, concomitant weakening of the X–S or X–Se bond in [OXSe]<sup>q</sup> occurs, but to different extents depending on the overall charge of the species. The bond weakening ranges from 25 to 155 kJ/mol, again with the larger values associated with a 2nd row X element. In the neutral OXS(Se) systems the bond strength changes essentially cancel but in the ionic [OXSe]<sup>±</sup> systems, the overall exchange enthalpy is dominated by the change in X–O bond strength.

When X = Ga<sup>-</sup>, the changes in bond strength in [OGaS(Se)]<sup>-</sup> compared to those in [OGaO]<sup>-</sup>, [SGaS]<sup>-</sup> and [SeGaSe]<sup>-</sup> are opposite to those found for X = B<sup>-</sup> and, in fact, for all other X but the likewise anionic Al<sup>-</sup>. The opposing factors dominant in the Ga<sup>-</sup> and B<sup>-</sup> species essentially cancel in the Al<sup>-</sup> species, and the exchange reactions are thermoneutral for the Al<sup>-</sup> species.

Table 3  
Stepwise bond enthalpies

Reaction	G2 (kJ/mol)	$\Delta BE^a$ (kJ/mol)
[OBS] <sup>-</sup> → [BS] <sup>-</sup> + O	808	88
[OBS] <sup>-</sup> → [BO] <sup>-</sup> + S	535	-54
[OBSe] <sup>-</sup> → [BSe] <sup>-</sup> + O	824	104
[OBSe] <sup>-</sup> → [BO] <sup>-</sup> + Se	473	-51
[SBSe] <sup>-</sup> → [BSe] <sup>-</sup> + S	596	7
[SBSe] <sup>-</sup> → [BS] <sup>-</sup> + Se	518	-6
[OBO] <sup>-</sup> → [BO] <sup>-</sup> + O	720	
[SBS] <sup>-</sup> → [BS] <sup>-</sup> + S	589	
[SeBSe] <sup>-</sup> → [BSe] <sup>-</sup> + Se	523	
[OAlS] <sup>-</sup> → [AlS] <sup>-</sup> + O	541	9
[OAlS] <sup>-</sup> → [AlO] <sup>-</sup> + S	453	-8
[OAlSe] <sup>-</sup> → [AlSe] <sup>-</sup> + O	542	10
[OAlSe] <sup>-</sup> → [AlO] <sup>-</sup> + Se	413	-5
[SAlSe] <sup>-</sup> → [AlSe] <sup>-</sup> + S	460	-1
[SAlS] <sup>-</sup> → [AlS] <sup>-</sup> + Se	419	1
[OAlO] <sup>-</sup> → [AlO] <sup>-</sup> + O	532	
[SAlS] <sup>-</sup> → [AlS] <sup>-</sup> + S	461	
[SeAlSe] <sup>-</sup> → [AlSe] <sup>-</sup> + Se	418	
[OGaS] <sup>-</sup> → [GaS] <sup>-</sup> + O	374	-60
[OGaS] <sup>-</sup> → [GaO] <sup>-</sup> + S	425	11
[OGaSe] <sup>-</sup> → [GaSe] <sup>-</sup> + O	376	-58
[OGaSe] <sup>-</sup> → [GaO] <sup>-</sup> + Se	394	15
[SGaSe] <sup>-</sup> → [GaSe] <sup>-</sup> + S	413	-1
[SGaSe] <sup>-</sup> → [GaS] <sup>-</sup> + Se	381	1
[OGaO] <sup>-</sup> → [GaO] <sup>-</sup> + O	435	
[SGaS] <sup>-</sup> → [GaS] <sup>-</sup> + S	414	
[SeGaSe] <sup>-</sup> → [GaSe] <sup>-</sup> + Se	380	
OCS → CS + O	670	141
OCS → CO + S	302	-137
OCSe → CSe + O	694	164
OCSe → CO + Se	217	-154
SCSe → CSe + S	460	21
SCSe → CS + Se	351	-20
OCO → CO + O	530	
SCS → CS + S	439	
SeCSe → CSe + Se	371	
OSiS → SiS + O	470	42
OSiS → SiO + S	284	-41
OSiSe → SiSe + O	477	50
OSiSe → SiO + Se	229	-51
SSiSe → SiSe + S	334	9
SSiSe → SiS + Se	271	-8
OSiO → SiO + O	427	
SSiS → SiS + S	326	
SeSiSe → SiSe + Se	280	
OGeS → GeS + O	340	34
OGeS → GeO + S	232	-35
OGeSe → GeSe + O	348	42
OGeSe → GeO + Se	189	-41
SGeSe → GeSe + S	274	7
SGeSe → GeS + Se	223	-7
OGeO → GeO + O	306	
SGeS → GeS + S	266	
SeGeSe → GeSe + Se	230	
[ONS] <sup>+</sup> → [NS] <sup>+</sup> + O	395	124
[ONS] <sup>+</sup> → [NO] <sup>+</sup> + S	272	-99
[ONSe] <sup>+</sup> → [NSE] <sup>+</sup> + O	426	154
[ONSe] <sup>+</sup> → [NO] <sup>+</sup> + Se	222	-115
[SNSe] <sup>+</sup> → [NSE] <sup>+</sup> + S	397	26
[SNSe] <sup>+</sup> → [NS] <sup>+</sup> + Se	316	-21
[ONO] <sup>+</sup> → [NO] <sup>+</sup> + O	271	
[SNS] <sup>+</sup> → [NS] <sup>+</sup> + S	371	
[SeNSE] <sup>+</sup> → [NSE] <sup>+</sup> + Se	337	
[OPS] <sup>+</sup> → [PS] <sup>+</sup> + O	330	53

Table 3 (Continued)

Reaction	G2 (kJ/mol)	$\Delta BE^a$ (kJ/mol)
[OPS] <sup>+</sup> → [PO] <sup>+</sup> + S	213	-31
[OPSe] <sup>+</sup> → [PSe] <sup>+</sup> + O	343	67
[OPSe] <sup>+</sup> → [PO] <sup>+</sup> + Se	182	-34
[SPSe] <sup>+</sup> → [PSe] <sup>+</sup> + S	253	9
[SPSe] <sup>+</sup> → [PS] <sup>+</sup> + Se	209	-7
[OPO] <sup>+</sup> → [PO] <sup>+</sup> + O	277	
[SPS] <sup>+</sup> → [PS] <sup>+</sup> + S	244	
[SePSe] <sup>+</sup> → [PSe] <sup>+</sup> + Se	216	
[OAsS] <sup>+</sup> → [AsS] <sup>+</sup> + O	199	47
[OAsS] <sup>+</sup> → [AsO] <sup>+</sup> + S	151	-27
[OAsSe] <sup>+</sup> → [AsSe] <sup>+</sup> + O	213	60
[OAsSe] <sup>+</sup> → [AsO] <sup>+</sup> + Se	133	-29
[SAsSe] <sup>+</sup> → [AsSe] <sup>+</sup> + S	186	8
[SAsSe] <sup>+</sup> → [AsS] <sup>+</sup> + Se	154	-7
[OAsO] <sup>+</sup> → [AsO] <sup>+</sup> + O	153	
[SAsS] <sup>+</sup> → [AsS] <sup>+</sup> + S	178	
[SeAsSe] <sup>+</sup> → [AsSe] <sup>+</sup> + Se	161	

<sup>a</sup> Bond dissociation enthalpy difference. See Eqs. (11) and (12) in the text for definitions.

Although exchanging O, S, and Se terminal atoms leads to changes in bond strength that are sometimes quite large (Table 3), the accompanying changes in bond length are moderate (Table S1). Comparing the bond lengths in [YXZ]<sup>q</sup> with those in [YXY]<sup>q</sup> and [ZXZ]<sup>q</sup> for X = C, Si, Ge and/or Y = S, Se shows that most bond lengths differ by no more than a few thousandths of an Å and that there is no clear pattern to these small changes. In contrast, for the cations the strengthening of the X–O bond is accompanied consistently by a lengthening of the bond and the weakening of the X–S(Se) bond is accompanied consistently by a shortening of the bond. For the anions, despite the differences in bond strength changes, all X–O bonds shorten and all X–S(Se) bonds lengthen. Addition of diffuse functions to the basis set lengthens the bonds in both the symmetric and antisymmetric anions, particularly when X = Ga<sup>-</sup>; consequently, the trends in the geometrical rearrangements are unaffected. As expected, the bond shortenings and elongations are larger for X elements from the second row and are smaller for Al<sup>-</sup> than for B<sup>-</sup> and Ga<sup>-</sup>. For this reason, our analysis of these results will be most applicable to X = N<sup>+</sup>, B<sup>-</sup> and Ga<sup>-</sup>.

The different trends observed for the anions and cations can be rationalized on the basis of two competing effects, which presumably effectively cancel in the neutrals. First, the lower symmetry of the [YXZ]<sup>q</sup> systems allows the  $\sigma_g$  and  $\sigma_u$  orbitals of the [YXY]<sup>q</sup>/[ZXZ]<sup>q</sup> systems to mix, forming sp hybrid orbitals on the central atom and stabilizing the molecular orbitals dominated by oxygen and destabilizing those dominated by sulfur or selenium. According to Bent's rules [41], since O is more electronegative than S and Se, there should be a concentration of p-character in the X hybrid orbitals directed toward O and a concentration of s-character in those directed toward S(Se), lengthening the bond to O and shortening the bond to S(Se). The X–O bond strengthens and the X–S(Se) bond weakens because forming the sp-hybrids on X increases the bonding character of the MOs dominated by oxygen and increases the antibonding character of the MOs dominated by S(Se). Second, concentrating p-character in the X-to-O orbitals makes X effectively more

electropositive with respect to O and should cause a removal of p-character in the O-to-X orbitals [41]. Likewise, an increase in the s-character of the X-to-S(Se) orbitals should lead to a loss of s-character in the S(Se)-to-X orbitals. Since the symmetry of the  $[YXZ]^q$  species precludes a change in the p-character of the lone pairs on O, S, and Se, if these rehybridizations occur there should be a transfer of s-electron density from the S(Se)-to-X orbitals to the O-to-X orbitals. Such rehybridizations of S, Se, and O would counteract the bond length changes described above. Moreover, with the higher energy S atomic orbitals mixing into the lower energy X–O molecular orbitals in a bonding way and the lower energy O atomic orbitals mixing into the higher energy X–S(Se) molecular orbitals in an antibonding way, the transfer of s-electron density would occur primarily in the bonding orbitals dominated by O. Thus, the X–O bond would strengthen and the X–S(Se) bond would weaken compared to their strengths in the  $[OXO]^q$ ,  $[SXS]^q$ , and  $[SeXSe]^q$  systems.

The NBO analysis indicates that, indeed, for all the systems studied the % s-character on the oxygen atom in the X–O bond and the % p-character on the sulfur or selenium atom in the X–S(Se) bond are larger in the triatomics with different terminal atoms than in those with identical terminal atoms (Table 4). Also, for all central atoms X except Al<sup>−</sup>, Ga<sup>−</sup> and Ge the X atom uses more p-character in the X–O bonds and more s-character in the X–S(Se) bonds in the asymmetric than in the symmetric systems. Note that the same types of changes in % s- and % p-character occur for the  $[SXS]^q$  systems, but to a much lesser extent (Table 4).

Since the contribution of the central atom to the  $\sigma$  bonds decreases in the order  $YXZ$  cation > neutral > anion (Table 4), it would be expected that the dominant effect would switch from the rehybridization of the orbitals on the central atom for the cations to the rehybridization of the orbitals on the terminal atoms for the anions. Such a switch does account for the observed changes in bond lengths and bond strengths for the  $YXZ$  cations, neutrals, and anions with  $X = B^-$ , compared to their  $YXY$  and  $ZXZ$  counterparts. It also accounts for the observed changes in bond lengths when  $X = Al^-$ ,  $Ga^-$ . The factors in the anions that lead to opposing bond strength changes in the  $B^-$  and  $Ga^-$  ions appear to be a stabilization of the X–S(Se) bond via a greater contribution of the sulfur or selenium atomic orbitals in the second highest occupied  $\sigma$  MO and a destabilization of the X–O bond via a greater contribution of the oxygen atomic orbitals to the highest occupied  $\sigma$  MO in the  $Ga^-$ -containing ions (Fig. 2).

### 3.2. $[HYXYH]^q$ and $[HYX]^q$ , $q = 0, +1$ , systems

Atomization enthalpies and geometrical parameters for those geometrical arrangements that are minima on the potential energy surfaces (PES) of the  $[HYXYH]^q$  and  $[HYX]^q$  systems are reported in Table 5 and Table S2, respectively. For these systems the G2 and G3 data deviate by as much as 21 kJ/mol (Table 5), but the mean absolute deviation is  $3 \pm 4$  kJ/mol. Of the eight arrangements considered for the pentaatomic species, only three are at minima. A twisted  $C_2$  structure **b** (Fig. 1) analogous

Table 4  
Molecular properties

Molecule	Bond	%X	%s on X	%s on Y, Z
[OBS] <sup>−</sup>	BO	21	42	57
	BS	39	57	26
[OBSe] <sup>−</sup>	BO	21	40	59
	BSe	42	59	22
[SBSe] <sup>−</sup>	BS	38	49	36
	BSe	43	51	29
[OBO] <sup>−</sup>	BO	23	50	46
[SBS] <sup>−</sup>	BS	39	50	34
[SeBSe] <sup>−</sup>	BSe	43	50	30
[OAlS] <sup>−</sup>	AlO	14	52	36
	AlS	24	47	22
[OAlSe] <sup>−</sup>	AlO	14	52	37
	AlSe	26	47	19
[SAlSe] <sup>−</sup>	AlS	25	49	28
	AlSe	28	50	24
[OAlO] <sup>−</sup>	AlO	14	50	29
[SAlS] <sup>−</sup>	AlS	26	50	27
[SeAlSe] <sup>−</sup>	AlSe	28	49	24
[OGaS] <sup>−</sup>	GaO	19	54	23
	GaS	28	46	18
[OGaSe] <sup>−</sup>	GaO	19	54	23
	GaSe	31	46	16
[SGaSe] <sup>−</sup>	GaS	29	50	23
	GaSe	32	50	19
[OGaO] <sup>−</sup>	GaO	19	50	18
[SGaS] <sup>−</sup>	GaS	30	50	22
[SeGaSe] <sup>−</sup>	GaSe	32	50	20
OCS	CO	34	42	44
	CS	58	58	21
OCSe	CO	33	40	46
	CSe	64	60	16
SCSe	CS	57	49	27
	CSe	63	51	20
OCO	CO	35	50	37
SCS	CS	58	50	26
SeCSe	CSe	63	50	21
OSiS	SiO	21	47	32
	SiS	40	51	16
OSiSe	SiO	20	47	34
	SiSe	44	52	13
SSiSe	SiS	40	49	21
	SiSe	45	50	17
OSiO	SiO	21	49	25
SSiS	SiS	40	49	20
SeSiSe	SiSe	44	50	17
OGeS	GeO	26	51	19
	GeS	42	49	13
OGeSe	GeO	25	50	20
	GeSe	46	49	10
SGeSe	GeS	42	50	17
	GeSe	47	50	13
OGeO	GeO	27	50	14
SGeS	GeS	42	50	16

Table 4 (Continued)

Molecule	Bond	%X	%s on X	%s on Y, Z
SeGeSe	GeSe	46	50	14
[ONS] <sup>+</sup>	NO	48	43	29
	NS	73	57	15
[ONSe] <sup>+</sup>	NO	48	42	30
	NSe	79	59	10
[SNSe] <sup>+</sup>	NS	72	48	18
	NSe	78	52	13
[ONO] <sup>+</sup>	NO	50	50	26
[SNS] <sup>+</sup>	NS	73	50	17
[SeNSe] <sup>+</sup>	NSe	77	50	13
[OPS] <sup>+</sup>	PO	30	46	25
	PS	55	53	11
[OPSe] <sup>+</sup>	PO	29	45	26
	PSe	61	54	8
[SPSe] <sup>+</sup>	PS	54	49	15
	PSe	60	51	11
[OPO] <sup>+</sup>	PO	31	49	19
[SPS] <sup>+</sup>	PS	54	50	14
[SePSe] <sup>+</sup>	PSe	59	50	12
[OAsS] <sup>+</sup>	AsO	34	49	15
	AsS	56	50	8
[OAsSe] <sup>+</sup>	AsO	33	49	16
	AsSe	61	51	6
[SAsSe] <sup>+</sup>	AsS	55	49	12
	AsSe	61	50	9
[OAsO] <sup>+</sup>	AsO	36	50	10
[SAsS] <sup>+</sup>	AsS	55	50	11
[SeAsSe] <sup>+</sup>	AsSe	60	50	9

Table 5

Calculated bond dissociation enthalpies  $D_m^\circ$  for HXYXH species<sup>a</sup>

Species	$D_m^\circ$ G2 (298 K)	$D_m^\circ$ G3 (298 K)
HNCNH, <b>b</b> , $C_2$	1951	1950
HNCNH, <b>a</b> , $D_{\text{och}}^b$	1883	1887
HPCPH, <b>b</b> , $C_2$	1496	1495
HPCPH, <b>a</b> , $D_{\text{och}}^b$	1005	1008
HAsCAsh, <b>b</b> , $C_2$	1307	
HAsCAsh, <b>a</b> , $D_{\text{och}}^b$	769	
HNC, $C_{\text{ov}}$	1217	1215
HPC, $C_{\text{ov}}$	716	713
HAsC, $C_{\text{ov}}$	618	
cyc-HNSiNH, <b>c</b> , $C_2$	1503	1482
HNSiNH, <b>b</b> , $C_2$	1560	1560
HNSiNH, <b>a</b> , $D_{\text{och}}^b$	1546	1546
cyc-HPSiPH, <b>d</b> , $C_s$	1256	1259
cyc-HPSiPH, <b>c</b> , $C_2$	1258	1257
HPSiPH, <b>b</b> , $C_2$	1216	1217
HPSiPH, <b>a</b> , $D_{\text{och}}^b$	854	855
cyc-HAsSiAsH, <b>d</b> , $C_s$	1130	
cyc-HAsSiAsH, <b>c</b> , $C_2$	1133	
HAsSiAsH, <b>b</b> , $C_2$	1090	
HAsSiAsH, <b>a</b> , $D_{\text{och}}^b$	673	
HNSi, $C_{\text{ov}}$	973	976
HPSi, $C_s$	702	703
HPSi, $C_{\text{ov}}^b$	658	659
HAsSi, $C_s$	641	
HAsSi, $C_{\text{ov}}$	582	
cyc-HNGeNH, <b>c</b> , $C_2$	1401	
HNGeNH, <b>b</b> , $C_2$	1376	
HNGeNH, <b>a</b> , $D_{\text{och}}^b$	1272	
cyc-HPGePH, <b>d</b> , $C_s$	1222	
cyc-HPGePH, <b>c</b> , $C_2$	1227	
HPGePH, <b>b</b> , $C_2$	1155	
HPGePH, <b>a</b> , $D_{\text{och}}^b$	744	
cyc-HAsGeAsH, <b>d</b> , $C_s$	1104	
cyc-HAsGeAsH, <b>c</b> , $C_2$	1108	
HAsGeAsH, <b>b</b> , $C_2$	1038	
HAsGeAsH, <b>a</b> , $D_{\text{och}}^b$	656	
HNGe, $C_{\text{ov}}$	863	
HPGe, $C_s$	663	
HPGe, $C_{\text{ov}}^b$	623	
HAsGe, $C_s$	606	
HAsGe, $C_{\text{ov}}$	552	
[HNNNH] <sup>+</sup> , <b>b</b> , $C_2$	2092	2089
[HNNNH] <sup>+</sup> , <b>a</b> , $D_{\text{och}}^b$	2007	2010
[HPNPH] <sup>+</sup> , <b>b</b> , $C_2$	1982	1977
[HPNPH] <sup>+</sup> , <b>a</b> , $D_{\text{och}}^b$	1376	1377
[HAsNAsH] <sup>+</sup> , <b>b</b> , $C_2$	1805	
[HAsNAsH] <sup>+</sup> , <b>a</b> , $D_{\text{och}}^b$	1126	
[HNN] <sup>+</sup> , $C_{\text{ov}}$	1521	1519
[HPN] <sup>+</sup> , $C_{\text{ov}}$	1128	1122
[HAsN] <sup>+</sup> , $C_{\text{ov}}$	1027	
[HNPNH] <sup>+</sup> , <b>b</b> , $C_2$	1592	1589
[HNPNH] <sup>+</sup> , <b>a</b> , $D_{\text{och}}^b$	1573	1568
cyc-[HPPPH] <sup>+</sup> , <b>d</b> , $C_s$	1414	1412
[HPPPH] <sup>+</sup> , <b>b</b> , $C_2$	1365	1360
[HPPPH] <sup>+</sup> , <b>a</b> , $D_{\text{och}}^b$	911	906
cyc-[HAsPAsH] <sup>+</sup> , <b>d</b> , $C_s$	1307	
[HAsPAsH] <sup>+</sup> , <b>b</b> , $C_2$	1268	
[HAsPAsH] <sup>+</sup> , <b>a</b> , $D_{\text{och}}^b$	733	
[HNP] <sup>+</sup> , $C_{\text{ov}}$	1101	1098
[HPP] <sup>+</sup> , $C_{2v}$	836	832
[HPP] <sup>+</sup> , $C_{\text{ov}}$	795	790
[HAsP] <sup>+</sup> , $C_s$	799	
[HAsP] <sup>+</sup> , $C_{\text{ov}}$	730	
[HNAsNH] <sup>+</sup> , <b>b</b> , $C_2$	1362	

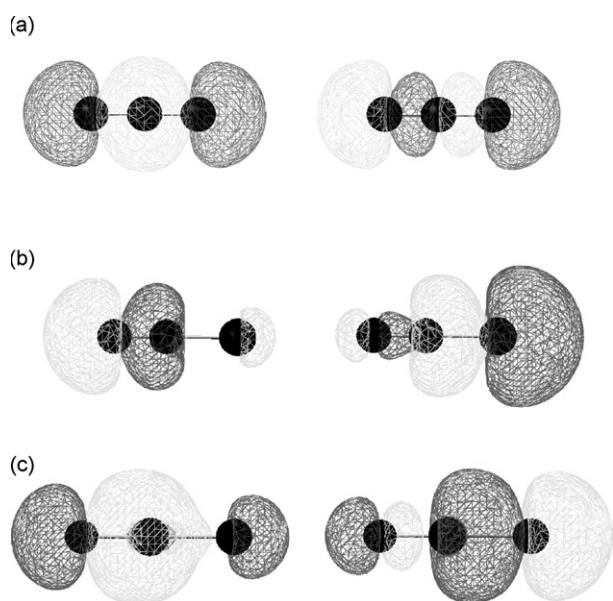


Fig. 2. Molecular orbital diagrams of the second highest occupied  $\sigma$  MO (left-hand side) and highest occupied  $\sigma$  MO (right-hand side) of (a) [OBO]<sup>−</sup>, (b) [OBS]<sup>−</sup>, and (c) [OGaS]<sup>−</sup>. Each anion is aligned as [OXY]<sup>−</sup>.



Table 5 (Continued)

Species	$D_m^\circ$ G2 (298 K)	$D_m^\circ$ G3 (298 K)
[HNAsNH] <sup>+</sup> , <b>a</b> , $D_{\infty h}^b$	1234	
cyc-[HPAsPH] <sup>+</sup> , <b>d</b> , $C_s$	1333	
[HPAsPH] <sup>+</sup> , <b>b</b> , $C_2$	1248	
[HPAsPH] <sup>+</sup> , <b>a</b> , $D_{\infty h}^b$	745	
cyc-[HAsAsAsH] <sup>+</sup> , <b>d</b> , $C_s$	1233	
[HAsAsAsH] <sup>+</sup> , <b>b</b> , $C_2$	1163	
[HAsAsAsH] <sup>+</sup> , <b>a</b> , $D_{\infty h}^b$	587	
[HNAs] <sup>+</sup> , $C_{\infty v}$	948	
[HPAs] <sup>+</sup> , $C_s$	748	
[HPAs] <sup>+</sup> , $C_{\infty v}$	719	
[HAsAs] <sup>+</sup> , $C_{2v}$	713	
[HAsAs] <sup>+</sup> , $C_{\infty v}$	660	

<sup>a</sup> Enthalpies in kJ mol<sup>-1</sup>. Total bond dissociation enthalpies for triatomic and pentaatomic systems.  $D_m^\circ(\text{HYXYH}) = \Delta_9 H^\circ$ . See Eqs. (9) and (10) in the text for definitions.

<sup>b</sup> Saddle point on the corresponding MP2(full)/6-31G(d) PES.

to that for allene [42–45] was found for all 18 neutral and ionic species examined. In addition, a more stable cyclic, orthogonal structure **d** was found when X and Y are 3rd or 4th row elements. For the neutral pentaatomics, the cyclic twisted  $C_2$  configuration **c** is also a minimum for all molecules other than HPCPH and HAsCAsH. Note the similarity in the stabilities of the two cyclic structures. Hydrogen-bridged  $C_{2v}$  or  $C_s$  geometries are lower in energy than linear  $C_{\infty v}$  geometries for the [HYX]<sup>q</sup> triatomics with Y and X from the 3rd or 4th row. The latter result is consistent with previous studies on [HPP]<sup>+</sup> [46–48], HPSi [49,50], HAsSi [51], and HAsGe [52]. The differences in stability between the linear and cyclic or bent arrangements range from 30 to 70 kJ/mol for the triatomic systems and from 40 to 85 kJ/mol for the pentaatomic systems, with the larger values associated with species with a central atom X from the 4th row. Although the linear  $D_{\infty h}$  structures **a** are 2nd- or occasionally even 4th-order saddle points on the PES of the [HYXYH]<sup>q</sup> systems, the atomization enthalpies for these structures are also given in Table 5 so that we can assess whether approximately constant bond dissociation enthalpy ratios are limited to linear structures.

Bending the HYX bond angle in [HAsP]<sup>+</sup> and [HPAs]<sup>+</sup> yields identical bridged structures. The P–H bond length in this mixed structure is about 0.02 Å shorter than that in [HPP]<sup>+</sup>, and the As–H bond length is about 0.03 Å longer than that in [HAsAs]<sup>+</sup> (Table S2). Thus, the hydrogen is more closely associated with the P than the As, but not to a large extent. Consistent with the relative ionization energies of P and As, about 50 kJ/mol more energy is required to separate the bridged cation into P<sup>+</sup>, As, and H than into P, As<sup>+</sup>, and H (Table 5) [53].

On the basis of earlier studies on HNCNH [54–57], HPCPH [58,59], HAsCAsH [58], HNSiNH [54,56], and HPSiPH [54], acyclic twisted structures **b** were expected for all of the additional HYXYH neutral and ionic species examined in this work. However, to our knowledge no one has previously identified stable cyclic, twisted  $C_2$ , or orthogonal  $C_s$  structures (**c** and **d**) for these species (Fig. 1). The [HYX]<sup>q</sup> systems have been investigated even more extensively, especially with respect to the relative stability of the [HYX]<sup>q</sup> and [HXY]<sup>q</sup> isomers and the

bridged versus linear structures [60–63]. Of particular note are the results of spectroscopic [64–66] and high-level theoretical studies that indicate that HPC is a saddle point on the PES of HCP [67–71]. That HPC is a minimum in this and other work appears to be an artifact of the MP2 method. Similar calculational evidence [47,48] demonstrates that [HPN]<sup>+</sup> and the  $C_{\infty v}$  structure for [HPP]<sup>+</sup> are also saddle points at higher levels of theory. In our work, discrepancies in the number of imaginary frequencies observed at the HF and MP2 levels for the  $C_{\infty v}$  structures of HAsSi, HAsGe and [HPAs]<sup>+</sup> suggest that those structures may be saddle points at higher levels of theory as well. Preliminary CCSD(T) and CASSCF(10,9) calculations with the cc-pVTZ basis set [72] performed in our laboratory for HNC, HPC, [HNN]<sup>+</sup>, [HPN]<sup>+</sup>, [HNP]<sup>+</sup>, and [HPP]<sup>+</sup> indicate that all of these species containing P have multireference character in the wave function. Similar results are expected for the species containing As. As will be discussed below, the bond dissociation enthalpy ratios derived from the atomization enthalpies of HPC and [HPN]<sup>+</sup> indicate that these systems may be problematic.

Higher levels of calculation are also required for the cyclic, twisted  $C_2$  structures **c** of the pentaatomic cations with X ≠ N. Structural and energetic data for these geometrical arrangements have been omitted from the tables since, again, the number of imaginary frequencies differ for the HF (zero) and MP2 (one) vibrational analyses. These data have been omitted for HNCNH **c** as well because, although it is a minimum at both levels of theory, it is some 400 kJ/mol less stable than configurations **a** and **b**.

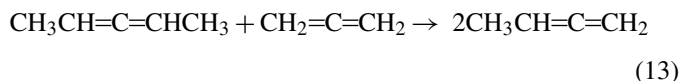
In accordance with Bent's rules [41], for the acyclic twisted  $C_2$  **b** pentaatomic neutrals and cations the YXY bond angle becomes more linear as Y switches from N to P to As (Table S2). The increase in bond angle is smallest for X=C, N<sup>+</sup>, perhaps because the overlap between the C–P (N<sup>+</sup>–P) and C–As (N<sup>+</sup>–As) atomic orbitals is the weakest. The changes in the remaining bond angles do not follow a consistent trend. For example, replacing the C in HNCNH with the more electropositive central atom Si decreases the magnitude of the NXN angle and increases the magnitude of the HNX angle. However, although the NXN angle continues to decrease in HNGeNH, the HNGe angle is the smallest of the three. Moreover, varying X leads to a different set of changes in the YXY and HYX angles when Y is P or As. For the linear [HYX]<sup>q</sup> triatomic molecules, the effect of X on the length of the Y–H bond shows similar inconsistencies (Table S2).

Unlike the [YXY]<sup>q</sup>, [YXZ]<sup>q</sup>, and [XY]<sup>q</sup> systems, generally both the pentaatomic HYXYH cations and the triatomic HYX cations have larger bond dissociation enthalpies than the corresponding neutrals (Tables 1 and 5, see previous section). One explanation for this enthalpy ordering is that the X–Y bond lengths are shorter in the cations than in the neutrals, which strengthens the bonding interactions in the cations. In addition, the relative energies of the [HYXYH]<sup>+</sup>/[HYX]<sup>+</sup> pairs parallel those of the related HYXYH/HYX pairs more closely than was observed for the [YXY]<sup>q</sup>/[XY]<sup>q</sup> and [YXZ]<sup>q</sup>/[XY]<sup>q</sup> pairs. Therefore, the trends in the bond dissociation enthalpy ratios should be at least somewhat different

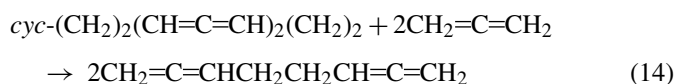
for the pentaatomic/triatomic versus triatomic/diatomic sets of 16-valence electron/10-valence electron pairs (see below).

### 3.3. Experimental thermochemistry

We find that there are few examples to discuss in the current section. The first reaction is



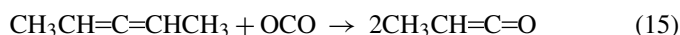
It is endothermic by  $1.0 \pm 1.6$  kJ/mol, i.e., this reaction enthalpy is truly indistinguishable from thermoneutrality. Again, this appears plausible. However, there are no other acyclic examples of substituted allenes for which this discussion applies. There is but one cyclic example, namely the reaction of 1,2,6,7-cyclodecatetraene [73,74] and allene to form 1,2,6,7-octatetraene [75].



Here, too, the reaction is very nearly thermoneutral, regardless of the stereochemistry of the cyclic species (DL versus meso) and accordingly of the amount of strain for this twisted, medium-sized ring.

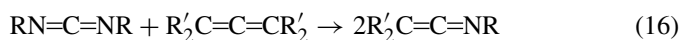
Dare we generalize to other cyclic and acyclic allenes? We are hesitant to do so given the paucity of thermochemical data for allene derivatives and those of the higher cumulenes [76,77]: all of the above thermochemical data for these species are from enthalpy of combustion and hydrogenation measurements of neutral hydrocarbons. Neither technique was used to obtain the enthalpy of formation of ketene (from ref. [6], using refs. [78–81] as the primary source) or for that matter has been used for any ketene derivative.

Consider reaction (15). This reaction is endothermic by ca. 92 kJ/mol where we have merely



accepted three suggested, but quite disparate, values for the enthalpy of formation of methylketene, all from the gas phase ion–molecule literature [82–84]. This value is rather different from that found for the parent allene and ketene above. However, it is to be remembered that both ketene and its methylketene have exhibited a wide range of suggested enthalpies of formation in the experimental literature. There are no other data from any experimental source for any other corresponding pair of allene and ketene.

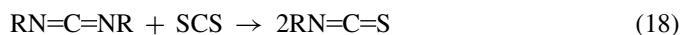
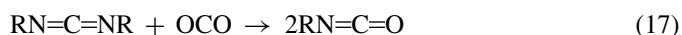
Consider now reactions involving carbodiimides and ketenimines, the first to be cited also involving the aforementioned allenes.



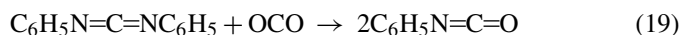
The sole ketenimine derivative for which we know the enthalpy of formation from experiment is a cyclic 1,2-didehydro-1H-azepine [85]. There is not enough information for determining the enthalpy of reaction (16) in the current case,

the requisite carbodiimide data being absent, and *a fortiori* for any other ketenimine.

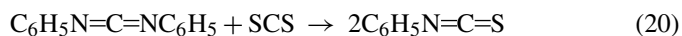
The situation appears not so bleak upon consideration of isocyanates and isothiocyanates, i.e., the following reactions.



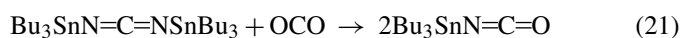
Enthalpy of formation data are known for carbodiimides with R = phenyl [86], isopropyl [6], and tributyltin [87]. Corresponding enthalpy of formation data are known for phenyl isocyanate [88–90] and isothiocyanate [91,92], and for tributyltin isocyanate [87].



With regards to diphenylcarbodiimide and phenyl isocyanate, we are thwarted because there is a 33 kJ/mol spread in measured values for the enthalpy of formation of the liquid phase of the latter (from –28 to –61 kJ/mol). Should we consider only the most recent value [90] on the grounds of currency and ignore the phase change enthalpy of CO<sub>2</sub> (no doubt quite small), we deduce a slightly exothermic reaction; an enthalpy of reaction of but –15 kJ/mol. Relatedly, for the liquid reaction we find an endothermic enthalpy of reaction of some +49 kJ/mol.



Indeed, we have used two nearly identical values for the enthalpy of formation of liquid phenyl isothiocyanate. However, our enthusiasm must be tempered because the two papers [91,92] are by the same author and date back to the beginning of the last century. We now turn to the tributyltin derivatives, both as liquids and the CO<sub>2</sub> as gas.



This reaction is endothermic by but some 17 kJ/mol.

None of the reactions we report are stunningly exothermic or endothermic. Unfortunately, however, even with a recent paper to provide guidance as to the energetics of phenyl isocyanate and isothiocyanate [93], we can only sadly acknowledge the paucity of thermochemical knowledge from the experimental literature on carbodiimides, isocyanates, and isothiocyanates. With that, we admit that we can say from experiment but very little about the various 16-valence electron species of interest in the current context.

### 3.4. Bond dissociation enthalpy ratios

#### 3.4.1. $[\text{YXZ}]^q$ , $q = -1, 0, +1$

The pattern discussed earlier with respect to the separation of properties when Y and Z are 3rd or 4th row elements compared to those when Y or Z is a 2nd row element is not reflected in the bond dissociation enthalpy ratios for the  $[\text{YXZ}]^q/[\text{XY}]^q/[\text{XZ}]^q$  systems (Eqs. (4), (6)–(8), Table 6). As was observed in our earlier work, there is little dependence on the group 13, 14, or 15 element X or on the group 16 elements Y and Z [2,3]. In fact, no non-zero exchange reaction enthalpy (Table 2) is large

Table 6

Bond dissociation enthalpy ratio  $D_m^\circ(\text{YXZ}^q)/[D_m^\circ(\text{XY}^q) + D_m^\circ(\text{XZ}^q)]^a$ 

Species	G2 ratio (298 K)	G3 ratio (298 K)	Expt. <sup>b</sup> ratio
[OBS] <sup>-</sup> /[BO] <sup>-</sup> /[BS] <sup>-</sup>	0.87	0.88	
[OBSe] <sup>-</sup> /[BO] <sup>-</sup> /[BSe] <sup>-</sup>	0.87		
[SBSe] <sup>-</sup> /[BS] <sup>-</sup> /[BSe] <sup>-</sup>	0.88		
[OAlS] <sup>-</sup> /[AlO] <sup>-</sup> /[AlS] <sup>-</sup>	0.87	0.87	
[OAlSe] <sup>-</sup> /[AlO] <sup>-</sup> /[AlSe] <sup>-</sup>	0.86		
[SAlSe] <sup>-</sup> /[AlS] <sup>-</sup> /[AlSe] <sup>-</sup>	0.86		
[OGaS] <sup>-</sup> /[GaO] <sup>-</sup> /[GaS] <sup>-</sup>	0.85		
[OGaSe] <sup>-</sup> /[GaO] <sup>-</sup> /[GaSe] <sup>-</sup>	0.85		
[SGaSe] <sup>-</sup> /[GaS] <sup>-</sup> /[GaSe] <sup>-</sup>	0.84		
OCS/CO/CS	0.77	0.78	0.78
OCSe/CO/CSe	0.77		
SCSe/CS/CSe	0.80		
OSiS/SiO/SiS	0.77	0.77	
OSiSe/SiO/SiSe	0.76		
SSiSe/SiS/SiSe	0.76		
OGeS/GeO/GeS	0.74		
OGeSe/GeO/GeSe	0.73		
SGeSe/GeS/GeSe	0.73		
[ONS] <sup>+</sup> /[NO] <sup>+</sup> /[NS] <sup>+</sup>	0.65	0.66	
[ONSe] <sup>+</sup> /[NO] <sup>+</sup> /[NSE] <sup>+</sup>	0.65		
[SNSe] <sup>+</sup> /[NS] <sup>+</sup> /[NSE] <sup>+</sup>	0.68		
[OPS] <sup>+</sup> /[PO] <sup>+</sup> /[PS] <sup>+</sup>	0.68	0.69	
[OPSe] <sup>+</sup> /[PO] <sup>+</sup> /[PSe] <sup>+</sup>	0.68		
[SPSe] <sup>+</sup> /[PS] <sup>+</sup> /[PSe] <sup>+</sup>	0.67		
[OAsS] <sup>+</sup> /[AsO] <sup>+</sup> /[AsS] <sup>+</sup>	0.64		
[OAsSe] <sup>+</sup> /[AsO] <sup>+</sup> /[AsSe] <sup>+</sup>	0.64		
[SAsSe] <sup>+</sup> /[AsS] <sup>+</sup> /[AsSe] <sup>+</sup>	0.65		

<sup>a</sup> G2 values include spin–orbit corrections for Ge and Se from reference [37].<sup>b</sup> Reference [6].

enough in magnitude to affect the expected trends in the calculated ratios  $[D_m^\circ(\text{YXZ}^q)]/[D_m^\circ(\text{XY}^q) + D_m^\circ(\text{XZ}^q)]$  (Table 6). The ratio for the  $[\text{YXZ}]^q/[\text{XY}]^q/[\text{XZ}]^q$  species never lies outside the ratios for the related  $[\text{YXY}]^q/[\text{XY}]^q$  and  $[\text{ZXX}]^q/[\text{XZ}]^q$  species and often lies between the latter two ratios [2,3]. As a result, the range of ratios is smaller for each set of asymmetric systems than for the related set of symmetric systems. For the  $[\text{YXZ}]^q/[\text{XY}]^q/[\text{XZ}]^q$  species the G2 ratio at 298 K is a nearly constant value of  $0.66 \pm 0.02$  for the cations,  $0.76 \pm 0.03$  for the neutrals and  $0.86 \pm 0.01$  for the anions. The corresponding ratios for the  $[\text{YXY}]^q/[\text{XY}]^q$  and  $[\text{ZXX}]^q/[\text{XZ}]^q$  pairs are  $0.66 \pm 0.03$ ,  $0.76 \pm 0.03$ , and  $0.86 \pm 0.02$ , respectively [2,3]. Therefore, the trend in the magnitudes of the calculated ratios cation < neutral < anion is also preserved. Utilizing G3 or G2(MP2) bond dissociation enthalpies or excluding the spin–orbit correction terms causes deviations of 0.01 or less in the bond dissociation enthalpy ratios (this work and references [2,3]). For OCS, the one YXZ system for which we have thermochemical data, the calculated and experimental [6] ratios  $[D_m^\circ(\text{OCS})]/[D_m^\circ(\text{CO}) + D_m^\circ(\text{CS})]$  are in excellent agreement (Table 6).

### 3.4.2. $[\text{HYXYH}]^q$ , $q = 0, +1$

In order to examine the possibility that the approximately constant bond dissociation enthalpy ratios obtained for the 16- and 10-valence electron neutral and ionic YXY/XY and

Table 7

Bond dissociation enthalpy ratios  $(D_m^\circ(\text{HYXYH}^q))/D_m^\circ(\text{HYX}^q)$ 

Species	G2 ratio (298 K)	G3 ratio (298 K)
cyc-HPSiPH/HPSi, $C_8/C_8$	0.89	0.90
cyc-HAsSiAsH/HAsSi, $C_8/C_8$	0.88	
cyc-HPGePH/HPGe, $C_8/C_8$	0.92	
cyc-HAsGeAsH/HAsGe, $C_8/C_8$	0.91	
cyc-HNSiNH/HNSi, $C_2/C_{\infty v}$	0.77	0.76
cyc-HPSiPH/HPSi, $C_2/C_8$	0.90	0.89
cyc-HAsSiAsH/HAsSi, $C_2/C_8$	0.88	
cyc-HNGeNH/HNGe, $C_2/C_{\infty v}$	0.81	
cyc-HPGePH/HPGe, $C_2/C_8$	0.93	
cyc-HAsGeAsH/HAsGe, $C_2/C_8$	0.91	
HNCNH/HNC, $C_2/C_{\infty v}$	0.80	0.80
HPCPH/HPC, $C_2/C_{\infty v}$	1.04	1.05
HAsCAsH/HAsC, $C_2/C_{\infty v}$	1.06	
HNSiNH/HNSi, $C_2/C_{\infty v}$	0.80	0.80
HPSiPH/HPSi, $C_2/C_8$	0.87	0.87
HAsSiAsH/HAsSi, $C_2/C_8$	0.85	
HNGeNH/HNGe, $C_2/C_{\infty v}$	0.80	
HPGePH/HPGe, $C_2/C_8$	0.87	
HAsGeAsH/HAsGe, $C_2/C_8$	0.86	
HNCNH/HNC, $D_{\text{och}}/C_{\infty v}^a$	0.77	0.78
HPCPH/HPC, $D_{\text{och}}/C_{\infty v}^a$	0.70	0.71
HAsCAsH/HAsC, $D_{\text{och}}/C_{\infty v}^a$	0.62	
HNSiNH/HNSi, $D_{\text{och}}/C_{\infty v}^a$	0.79	0.79
HPSiPH/HPSi, $D_{\text{och}}/C_{\infty v}^{a,b}$	0.65	0.65
HAsSiAsH/HAsSi, $D_{\text{och}}/C_{\infty v}^a$	0.58	
HNGeNH/HNGe, $D_{\text{och}}/C_{\infty v}^a$	0.74	
HPGePH/HPGe, $D_{\text{och}}/C_{\infty v}^{a,b}$	0.60	
HAsGeAsH/HAsGe, $D_{\text{och}}/C_{\infty v}^a$	0.59	
cyc-[HPPPH] <sup>+</sup> /[HPP] <sup>+</sup> , $C_8/C_{2v}$	0.85	0.85
cyc-[HAsPAsH] <sup>+</sup> /[HAsP] <sup>+</sup> , $C_8/C_8$	0.82	
cyc-[HPAsPH] <sup>+</sup> /[HPAs] <sup>+</sup> , $C_8/C_8$	0.89	
cyc-[HAsAsAsH] <sup>+</sup> /[HAsAs] <sup>+</sup> , $C_8/C_{2v}$	0.87	
[HNNNH] <sup>+</sup> /[HNN] <sup>+</sup> , $C_2/C_{\infty v}$	0.69	0.69
[HPNPH] <sup>+</sup> /[HPN] <sup>+</sup> , $C_2/C_{\infty v}$	0.88	0.88
[HAsNAsH] <sup>+</sup> /[HAsN] <sup>+</sup> , $C_2/C_{\infty v}$	0.88	
[HNPNH] <sup>+</sup> /[HNP] <sup>+</sup> , $C_2/C_{\infty v}$	0.72	0.72
[HPPPH] <sup>+</sup> /[HPP] <sup>+</sup> , $C_2/C_{2v}$	0.82	0.82
[HAsPAsH] <sup>+</sup> /[HAsP] <sup>+</sup> , $C_2/C_8$	0.79	
[HNAsNH] <sup>+</sup> /[HNAs] <sup>+</sup> , $C_2/C_{\infty v}$	0.72	
[HPAsPH] <sup>+</sup> /[HPAs] <sup>+</sup> , $C_2/C_8$	0.83	
[HAsAsAsH] <sup>+</sup> /[HAsAs] <sup>+</sup> , $C_2/C_{2v}$	0.82	
[HNNNH] <sup>+</sup> /[HNN] <sup>+</sup> , $D_{\text{och}}/C_{\infty v}^a$	0.66	0.66
[HPNPH] <sup>+</sup> /[HPN] <sup>+</sup> , $D_{\text{och}}/C_{\infty v}^a$	0.61	0.61
[HAsNAsH] <sup>+</sup> /[HAsN] <sup>+</sup> , $D_{\text{och}}/C_{\infty v}^a$	0.55	
[HNPNH] <sup>+</sup> /[HNP] <sup>+</sup> , $D_{\text{och}}/C_{\infty v}^a$	0.71	0.71
[HPPPH] <sup>+</sup> /[HPP] <sup>+</sup> , $D_{\text{och}}/C_{\infty v}^a$	0.57	0.57
[HAsPAsH] <sup>+</sup> /[HAsP] <sup>+</sup> , $D_{\text{och}}/C_{\infty v}^a$	0.50	
[HNAsNH] <sup>+</sup> /[HNAs] <sup>+</sup> , $D_{\text{och}}/C_{\infty v}^a$	0.65	
[HPAsPH] <sup>+</sup> /[HPAs] <sup>+</sup> , $D_{\text{och}}/C_{\infty v}^a$	0.52	
[HAsAsAsH] <sup>+</sup> /[HAsAs] <sup>+</sup> , $D_{\text{och}}/C_{\infty v}^a$	0.44	

<sup>a</sup>  $D_{\text{och}}$  structure is a saddle point on the corresponding MP2(full)/6-31G(d) PES.<sup>b</sup>  $C_{\infty v}$  structure is a saddle point on the corresponding MP2(full)/6-31G(d) PES.

YXZ/XY/XZ species arises from their linear geometries, we evaluated the analogous ratios  $(D_m^\circ(\text{HYXYH}^q))/D_m^\circ(\text{HYX}^q)$  for the cationic and neutral  $D_{\text{och}}/C_{\infty v}$  structures of HYXYH/HYX (Eqs. (9) and (10), Table 7). Note that for all of the ratios collected in the table, the G2 and G3 data again differ by no more than 0.01. This observation also holds for the G2(MP2) data (not shown). The results clearly demonstrate

that the observed near constancy in the bond dissociation enthalpy ratios cannot be rationalized simply on the basis of linear geometries. The ratio ranges (Table 7) for the  $D_{\text{och}}/C_{\infty\text{v}}$  structures are much larger than found in our previous work [2,3], at 0.27 for the cations and 0.21 for the neutrals. The average ratio for the cationic species is now  $0.58 \pm 0.09$  and that for the neutral species is now  $0.67 \pm 0.08$ . For both sets of data, there is a tendency for the ratio to decrease as Y progresses down group 15 and as X progresses down group 14 or 15, although the trend is less consistent with respect to the change in X.

Consider now the more stable pairs of cyclic  $C_s$  or  $C_2$  structures for  $[\text{HYXYH}]^q$  and bridged  $C_{2v}$  or  $C_s$  structures for  $[\text{HYX}]^q$ ,  $X = \text{P}^+, \text{As}^+, \text{Si}, \text{Ge}$  and  $Y = \text{P}, \text{As}$ . The data in Table 7 show that the bond dissociation enthalpy ratios are not only approximately constant, but are similar in magnitude for the cationic and neutral species. The ratio that differs most noticeably from the others is  $\langle D_{\text{m}}^{\circ}(\text{HAsPAsH}^+) \rangle / D_{\text{m}}^{\circ}(\text{PAsH}^+)$  because of the complication that the bridged structure is identical for  $[\text{HAsP}]^+$  and  $[\text{HPAs}]^+$ . Since the hydrogen is more closely associated with the phosphorus than the arsenic in this bridged structure (Table S2), we have reevaluated  $\langle D_{\text{m}}^{\circ}(\text{HAsPAsH}^+) \rangle / D_{\text{m}}^{\circ}(\text{HAsP}^+)$  with  $D_{\text{m}}^{\circ}(\text{HAsP}^+)$  for the linear ion and obtain a ratio of 0.90. The mean value for the bond dissociation enthalpy ratios of the original 12 pairs is  $0.89 \pm 0.03$ , which improves slightly to  $0.90 \pm 0.02$  with the linear  $[\text{HAsP}]^+$ .

Finally, bond dissociation enthalpy ratios have been calculated for all 18 acyclic, twisted  $C_2$  structures for the pentaatomic species together with the more stable bridged or linear structure for the relevant triatomic species (Table 7). In this case, some unexpectedly high ratios are found, especially for the HPCPH/HPC and HAsCAsH/HAsC systems. That the ratios are too large is consistent with unusually low stabilities for the triatomics and could be used as an indicator that these systems may be problematic and should be reexamined at higher calculational levels. Although the discrepancies are less severe for the  $[\text{HPNPH}]^+ / [\text{HPN}]^+$  and  $[\text{HAsNAsH}]^+ / [\text{HAsN}]^+$  cation pairs, our results also suggest that  $[\text{HAsN}]^+$ , as well as  $[\text{HPN}]^+$  [47,48], may be a saddle point at higher levels of theory. For the remaining acyclic neutral and cationic pairs, there is a more definite dependence on Y than has been seen for any of the other systems we have studied. This dependence on Y is also observed for the neutral cyclic, twisted  $C_2$  structures (Table 7). When  $Y = \text{N}$ , the bond dissociation enthalpy ratios are lower by as much as 0.16 compared to the ratios for  $Y = \text{P}, \text{As}$ , with the larger gaps associated with the acyclic cations and cyclic neutrals. For the acyclic  $Y = \text{N}$  systems, the ratios for the cations are again about 0.1 smaller in magnitude than the ratios for the neutrals. In contrast, when X is a 3rd or 4th row element and  $Y = \text{P}, \text{As}$ , the two sets of ratios are similar in magnitude and when grouped together yield a mean ratio of  $0.84 \pm 0.03$ . The ratio is  $0.79 \pm 0.07$  when all of the  $C_2$  cation ratios are averaged and  $0.88 \pm 0.10$  when all of the acyclic  $C_2$  neutral ratios are averaged. Excluding the four suspect systems improves the ratios to  $0.77 \pm 0.06$  and  $0.84 \pm 0.03$  for the cations and neutrals, respectively. Thus, combining the neutral systems and the

four cationic systems with  $X, Y = \text{P}, \text{As}$  has very little effect on the average ratio for the neutral systems.

At this point the calculational data suggest that as long as valence isoelectronic species with similar geometries are grouped together, the bond dissociation enthalpy ratios will be nearly constant. One significant difference in the  $[\text{HYXYH}]^q / [\text{HYX}]^q$  systems when  $Y = \text{N}$  is that  $[\text{HNX}]^q$  has a linear rather than a bridged geometry, which may also help to account for the distinctly different ratios observed for the cations and neutrals when  $Y = \text{N}$ .

### 3.5. Summary

In summary, it appears as though corresponding isovalent isoelectronic species  $\text{YXY}, \text{YXZ}$ , and  $\text{HYXYH}$  formed from central atoms (X) of the 3rd and 4th rows are very similar to each other and different from the corresponding species with 2nd row central atoms—what we say about species with Al applies to Ga but less to B, what we say about Si applies to Ge but less to C, and likewise P to As but less to N. Isovalent isoelectronic species with 3rd and 4th row terminal atoms S and Se are also similar, and likewise different from those with the 2nd row O. This is not particularly surprising: consider the normally asserted trends in electronegativity, atomic radii and strength of multiple bonding.

Using our computationally derived numbers we find in our analysis that we can successfully interpolate bond length trends and the energy ratio for the neutral species  $\text{YXY}, \text{YXZ}$  and the related  $\text{XY}, \text{XZ}$  from those of the adjacent cation and anion. For example, we may derive results for  $\text{OCS}$  from  $[\text{OBS}]^-$  and  $[\text{ONS}]^+$ ,  $\text{SiS}$  from  $[\text{AIS}]^-$  and  $[\text{PS}]^+$ . For the cations we plausibly present the Lewis structures  $\text{Y}=\text{X}^+=\text{Y}$  and  $\text{X}\equiv\text{Y}^+$ . Double bonds are expected to be longer than triple bonds and indeed, for the cations, the diatomic often has the shorter bond. Double bonds are also generally weaker than triple bonds, and so the energy ratio is relatively small. Where  $\pi$  bonds are expected to be strong, i.e., ions with nitrogen, this effect will be amplified. For the case of anions where  $\pi$  bonding is expected to be strong (i.e., boron-containing species), the energy ratio again will be small. However, for the majority of cases, we may expect the considerable importance of singly bonded resonance structures,  $\text{Y}^--\text{X}^+-\text{Y}^-$  and  $\text{X}-\text{Y}^-$ . Because the former contains the central element positively charged and also in a higher oxidation state, we may expect the triatomic to have the shorter bond. The ratio is accordingly expected to be larger than for the corresponding cations because the bonds are formally single, and additionally strengthened by charge attraction in the triatomic.

Indeed, we find confirmation of all of these trends including the values for C are roughly the average of those of B and N, Si the average of Al and P, and Ge very similar to Si as well as the average of Ga and As.

For the  $\text{HYXYH}$  systems, with  $Y = \text{N}$ , regardless of X, the above analysis also holds in that the ratio for the cations is smaller than that for the neutrals and both sets of ratios are smaller than those for  $Y = \text{P}, \text{As}$ . However, for the latter Y elements, for which the triatomic  $\text{HYX}$  is bridged rather than linear, the ratios for the cations and neutrals differ little in magnitude. It remains to be tested whether similar results will be found for the

anions. There are also several ratios that are unexpectedly high, which may be used as an indicator that the relevant triatomic species may be problematic and should be studied at a higher level of theory.

### Supporting information available

Bond lengths for the YXZ systems (Table S1) and geometrical parameters for the HXYXH and HXY systems (Table S2).

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2007.03.005.

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