

10-15-2005

Computational Study of Sulfur Atom-Transfer Reactions from Thiiranes to ER₃ (E = As, P; R = CH₃, Ph)

Abdellatif Ibdah
Iowa State University

James H. Espenson
Iowa State University

William S. Jenks
Iowa State University, wsjenks@iastate.edu

Follow this and additional works at: http://lib.dr.iastate.edu/chem_pubs

 Part of the [Organic Chemistry Commons](#), [Other Chemistry Commons](#), and the [Polymer Chemistry Commons](#)

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/chem_pubs/159. For information on how to cite this item, please visit <http://lib.dr.iastate.edu/howtocite.html>.

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

Computational Study of Sulfur Atom-Transfer Reactions from Thiiranes to ER₃ (E = As, P; R = CH₃, Ph)

Abstract

Computational estimates have been made for the PS and AsS bond strengths in triphenylphosphine sulfide and triphenylarsine sulfide, on the basis of G3 calculations for the methyl analogues and isodesmic-exchange reactions. Also, with the performance of the G3 method level for related compounds taken into consideration, the best estimates are 82 and 68 kcal/mol, respectively. While the value for triphenylarsine sulfide is within 2 kcal/mol of the single experimental estimate, that for triphenylphosphine sulfide is lower by 6 kcal/mol. (Capps, K. B.; Wixmerten, B.; Bauer, A.; Hoff, C. D. *Inorg. Chem.* **1998**, *37*, 2861–2864.) Despite virtually identical electronegativities of P and As, it is found that there is greater charge separation in the PS bond. It is found that S atom transfer from thiiranes to arsines is exothermic.

Disciplines

Chemistry | Organic Chemistry | Other Chemistry | Polymer Chemistry

Comments

Reprinted (adapted) with permission from *Inorganic Chemistry*, 44(23); 8426-8432. Doi: [10.1021/ic051228w](https://doi.org/10.1021/ic051228w). Copyright 2005 American Chemical Society.

Rights

One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

Computational Study of Sulfur Atom-Transfer Reactions from Thiiranes to ER₃ (E = As, P; R = CH₃, Ph)

Abdellatif Ibdah, James H. Espenson, and William S. Jenks*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

Received July 22, 2005

Computational estimates have been made for the P=S and As=S bond strengths in triphenylphosphine sulfide and triphenylarsine sulfide, on the basis of G3 calculations for the methyl analogues and isodesmic-exchange reactions. Also, with the performance of the G3 method level for related compounds taken into consideration, the best estimates are 82 and 68 kcal/mol, respectively. While the value for triphenylarsine sulfide is within 2 kcal/mol of the single experimental estimate, that for triphenylphosphine sulfide is lower by 6 kcal/mol. (Capps, K. B.; Wixmerten, B.; Bauer, A.; Hoff, C. D. *Inorg. Chem.* **1998**, *37*, 2861–2864.) Despite virtually identical electronegativities of P and As, it is found that there is greater charge separation in the P=S bond. It is found that S atom transfer from thiiranes to arsines is exothermic.

Introduction

The fundamental chemistry of second and third row main group elements is of particular interest to organic chemists because of the shortcomings of ordinary valence-bond descriptions of their oxides and sulfides. Even molecular orbital calculations have resulted in interpretations that are dependent on the various schemes used to create localized-looking bonds or bond orders. This also manifests itself in the varying and inconsistent ways that such bonds are drawn in the literature. Despite the close analogy, phosphine oxide and sulfonyl functions are almost universally represented as apparently double bonds (e.g., R₃P=O), but the sulfoxide is variously represented as S=O, S⁺–O[–], or S → O.¹ While it is clear that none of these interactions is a “classic” double bond, consisting of a simple strong sigma and pi interaction, detailed descriptions still are not well put in the conventional language of organic chemists. Several computational studies suggest that the best description of such bonds is a polar sigma bond, supplemented by additional electrostatic bonding as evidenced by distorted lone pairs on the oxo atom or a single strongly polarized bond, depending, again, on the computational model used and the exact type of compound being studied.^{2–11}

Of practical interest is the corresponding bond strength because of the utility of such compounds as oxygen or sulfur sinks in atom-transfer reactions. The extraordinary P–O bond dissociation energy of 130 kcal/mol for Ph₃PO¹² has led to its very common use in such chemistry.¹³ For example, in experimental work complementary to these studies, it has been found that both Ph₃P and Ph₃As both react spontaneously in oxygen atom-transfer reactions. However, these reactions present nearly prohibitive kinetic barriers; for that reason the actual chemistry has been advanced by monomeric and dimeric oxorhenium(V) catalysts, as has been reviewed recently.¹⁴

Experimental values for the bond dissociation energies for arsine sulfides are, not surprisingly, considerably more sparse than those for more common functions, such as phosphine oxides. To the best of our knowledge, only a single value

* To whom correspondence should be addressed. E-mail: wsjenks@iastate.edu.

- (1) Brief but excellent summaries of the primary and review literature are given in the Dobado references cited below.
- (2) Schmidt, M. W.; Yabushita, S.; Gordon, M. S. *J. Phys. Chem.* **1984**, *88*, 382–389.
- (3) Schmidt, M. W.; Gordon, M. S. *Can. J. Chem.* **1985**, *63*, 1609–1615.

- (4) Gilheany, D. G. *Chem. Rev.* **1994**, *94*, 1339–1374.
- (5) Dobado, J. A.; Martinez-Garcia, H.; Molina, J. M.; Sundberg, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 8461–8471.
- (6) Dobado, J. A.; Martinez-Garcia, H.; Molina, J. M.; Sundberg, M. R. *J. Am. Chem. Soc.* **1999**, *121*, 3156–3164.
- (7) Dobado, J. A.; Martinez-Garcia, H.; Molina, J. M.; Sundberg, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1144–1149.
- (8) Ciolowski, J.; Mixon, S. T. *Inorg. Chem.* **1993**, *32*, 3209–3216.
- (9) Chesnut, D. B. *J. Phys. Chem. A* **2003**, *107*, 4307–4313.
- (10) Chesnut, D. B.; Quin, L. D.; Seaton, P. J. *Magn. Res. Chem.* **2004**, *42*, S20–S25.
- (11) Chesnut, D. B.; Quin, L. D. *J. Comput. Chem.* **2004**, *25*, 734–738.
- (12) Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, 2003.
- (13) That of trimethylphosphine oxide is 139 kcal/mol, also according to ref 12.
- (14) Espenson, J. H. *Coord. Chem. Rev.* **2005**, *249*, 329–341.

Table 1. R₃E=S BDEs Estimated by Hoff and Coworkers¹⁵

compound	BDE (kcal/mol)
Me ₃ P=S	94
Ph ₃ P=S	88
Ph ₃ As=S	70

exists, based on the heat of reaction of Ph₃As with S₈.¹⁵ It and two other related estimates, are given in Table 1.

Given the paucity of data and our interest in these compounds for S atom-transfer reactions, we were prompted to pursue a computational investigation into the thermochemistry of these atom transfer reactions, which we report here. Computational challenges posed by the elements, types of functional groups, and sizes of molecules involved are addressed with smaller, but nonetheless realistic, molecules and results are compared to the experimental report.

Computational Methods

Computations, as described in the text, were carried out using ab initio methods, the hybrid density functional B3LYP, and the empirically corrected "Gaussian theory" methods G2^{16–18} and G3.^{19–21} The G2 calculations were carried out using the Gaussian 94 package of ab initio programs²² and the G3 calculations were carried out using the Gaussian 03 package.²³ All other computations were carried out using GAMESS.²⁴ All quoted energies are without

temperature correction (i.e., at 0 K). All structures were confirmed as minima by calculating vibrational frequencies, and zero-point energies are unscaled. All basis sets used were of the Pople type as implemented in GAMESS,^{25,26} with the exception of the G2 and G3 calculations themselves and the use of the G3Large basis set, available for download from <http://chemistry.anl.gov/compmat/comptherm.htm>. Atomic charges and bond order indices were obtained from the generalized MP2 density matrix in GAMESS.^{27–29}

Results

Initial stages of the investigation were used to determine practical levels of theory to obtain energies using reactions with small molecules. Although it is by no means perfect,²¹ G3 theory usually produces chemically accurate thermochemical results for the great majority of mid-sized organic molecules (≤10 non-H atoms). It was taken as the benchmark calculation for comparison to other types of computations. For reasons to be discussed below, G2 theory, which is more expensive and generally not quite as reliable, was also used, although it was not intended as a final solution. For all other calculations, fixed geometries, calculated at the MP2/6-31++G(d,p) level, were used. Zero-point energies were calculated at the same level as the optimization. Enthalpies, taken as the sum of the electronic and zero-point energies, for several reactions are reported in Table 2. Heats of formation, calculated by the atomization method using the G3 data, are given in Table 3. It should be noted that calculations for H₃P and H₃As and their respected sulfides are included because H₃P and H₃As are compounds for which good experimental heats of formation are known. However, the corresponding sulfides are not experimentally known; they are included for completeness throughout the text.

Given that the experimental data for atom-transfer chemistry mainly concern the use of triphenylphosphine and triphenylarsine, rather than the smaller methyl derivatives, computations had to be done with these larger compounds. Because the G3 calculations scale approximately as *n*,⁷ it is not plausible to perform them on molecules with as many as 20 non-hydrogen atoms (e.g., Ph₃PO) at this time. Thus, more affordable methods were used to do the calculations shown in Table 4. The trends from the data in Table 2 were then used to guide the interpretation. Structures were optimized and zero-point energies were obtained at the MP2 level with the following mixed basis sets: 6-31+G(d) for sulfur, 6-31G(d) for As and P, and 6-31G for C and H. Single-point energies were calculated using 6-31G(d) for C and H and G3Large on As, S, and P. Zero-point energies for reactions 10–12 were obtained at the RHF level, rather than MP2.

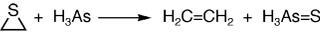
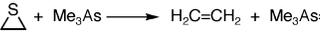
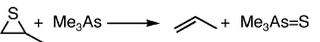
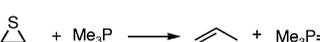
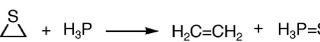
Discussion

Methods. Of the various sulfides and oxides of the phosphorus and arsenic, the factors that affect the ability to

- (15) Capps, K. B.; Wixmerten, B.; Bauer, A.; Hoff, C. D. *Inorg. Chem.* **1998**, *37*, 2861–2864.
- (16) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221–7230.
- (17) Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1992**, *96*, 9030–9034.
- (18) Curtiss, L. A.; Redfern, P. C.; Smith, B. J.; Radom, L. *J. Chem. Phys.* **1996**, *104*, 5148–5152.
- (19) Curtiss, L. A.; Redfern, P. C.; Rassolov, V.; Kedziora, G.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 9287–9295.
- (20) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764–7776.
- (21) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 7374–7383.
- (22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.
- (23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (24) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, N.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.

- (25) Rassolov, V. A. R.; Pople, J. A.; Ratner, M. A.; Windus, T. L. *J. Chem. Phys.* **1998**, *109*, 1223–1229.
- (26) Rassolov, V. A. R.; Mark, A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comput. Chem.* **2001**, *22*, 976–984.
- (27) Giambiagi, M.; Giambiagi, M.; Gempel, D. R.; Heymann, C. D. *J. Chim. Phys. Phys.-Chim. Biol.* **1975**, *72*, 15–22.
- (28) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270–274.
- (29) Mayer, I. *Chem. Phys. Lett.* **1985**, *117*, 396.

Table 2. Heats of Reaction (kcal/mol)^a

		Expt ^b	G3	G2	MP2(full) 6-31++G(d,p) G3L for As, S, P	MP2(full) G3Large	MP2 G3Large	B3LYP G3Large
1	$\text{H}_3\text{As}=\text{S} + \text{Me}_3\text{As} \longrightarrow \text{H}_3\text{As} + \text{Me}_3\text{As}=\text{S}$		-21.1	-17.6	-22.7	-21.2	-20.3	-17.9
2			12.0	9.7	15.0	13.2	10.4	9.6
3			15.0	12.1	18.5	16.3	16.8	11.2
4			-9.1	-7.9	-7.7	-8.0	-9.9	-8.2
5			-6.2	-5.6	-4.2	-4.8	-6.7	-6.6
6			-1.2	-3.0	-2.3	-3.5	-3.2	-3.2
7			-27.1	-24.3	-26.4	-26.9	-27.4	-26.4
8			-24.6	-22.0	-22.9	-23.7	-24.2	-24.8
9			-3.4	-2.6		-3.1	-4.1	-6.6

^a All G3 and G2 geometries as per the literature technique; all other energy calculations at the MP2/6-31++G(d,p) geometry. All values are calculated for 0 K. ^b Heats of formation of ethylene, ethylene sulfide, propylene, and propylene sulfide: 12.54 ± 0.1 , 19.9 ± 0.5 , 4.8 ± 0.2 , and 11.0 ± 0.5 . (refs 30 and 31).

Table 3. Heats of Formation (kcal/mol) Calculated by Atomization at 0 K^a

	ΔH_f (0 K), exptl ^a	ΔH_f (0 K), G3
H ₃ As	17.8	19.1
H ₃ As=S		38.4
Me ₃ As		-2.7
Me ₃ As=S		-4.5
H ₃ P	3.2	5.0
H ₃ P=S		8.9
Me ₃ P		-17.5
Me ₃ P=S		-37.3

^a Experimental values obtained from refs 32 and 33.

get correct energies are probably best understood for sulfur oxides because of the importance of SO₂ as an atmospheric species and its relatively small size. It is now well-known that getting the correct absolute energy for compounds such as SO₂, SO₃, and DMSO is not a trivial matter. Indeed, the error in the heat of formation for SO₂ is among the worst outliers in the G3 test set (error = -3.8 kcal/mol, with stability underestimated), though DMSO falls within the “normal” range of <2 kcal/mol error.²⁰ Dimethyl sulfone behaves relatively well at the G3 level itself (error = -2.3 kcal/mol) but is much worse at, for example, G3(MP2) (error = -4.1 kcal/mol).²¹ SO₃, POCl₃, and SO₂Cl₂ are also among the outliers, but all have deviations of the same sign (negative) and magnitude of 3–5 kcal/mol.²¹ Notably, the stability of these compounds is consistently underestimated.

While the computational method clearly must be sufficiently rigorous, the basis set is now understood to be critical in recovering the error. For example, the CCSD(T)

method had a relatively large (ca. 6 kcal/mol) error in the binding energy of SO₂ even when the usually reliable correlation-consistent basis sets of Dunning³⁴ (cc-pVnZ) were extrapolated to the complete basis set limit.³⁵ A “fix” was found by the inclusion of very tight d core-polarization functions. This approach has been examined explicitly for SO₂^{36–38} and SO₃^{39–41} and other molecules (see, for example, refs 42–47). Although several smaller contributions to the

- (30) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2003; <http://www.webbook.nist.gov>.
- (31) Mackle, H.; O'Hare, P. A. G. *Tetrahedron* **1963**, *19*, 1223–1229.
- (32) Bercowitz, J. *J. Chem. Phys.* **1988**, *89*, 7065–7066.
- (33) Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460–17464.
- (34) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (35) Bauschlicher, C. W., Jr.; Partridge, H. *Chem. Phys. Lett.* **1995**, *240*, 533–540.
- (36) Wilson, A. K.; Dunning, T. H., Jr. *J. Chem. Phys.* **2003**, *119*, 11712–11714.
- (37) Martin, J. M. L. *J. Chem. Phys.* **1998**, *108*, 2791–2800.
- (38) Wang, N. X.; Wilson, A. K. *J. Phys. Chem. A* **2003**, *107*, 6720–6724.
- (39) Bell, R. D.; Wilson, A. K. *Chem. Phys. Lett.* **2004**, *394*, 105–109.
- (40) Martin, J. M. L. *Chem. Phys. Lett.* **1999**, *310*, 271–276.
- (41) Martin, J. M. L. *Spectrochim. Acta A* **1999**, *55*, 709–718.
- (42) Wang, L.; Zhang, J. *THEOCHEM* **2002**, *581*, 129–138.
- (43) Ventura, O. N.; Kieninger, M.; Denis, P. A.; Cachau, R. E. *Chem. Phys. Lett.* **2002**, *355*, 207–213.
- (44) Ventura, O. N.; Kieninger, M.; Denis, P. A. *J. Phys. Chem. A* **2003**, *107*, 518–521.
- (45) Ruttink, P. J. A.; Burgers, P. C.; Trikoupis, M. A.; Terlouw, J. K. *Chem. Phys. Lett.* **2001**, *342*, 447–451.
- (46) Wesolowski, S. S.; Brinkmann, N. R.; Valeev, E. F.; Schaefer, H. F., III; Repasky, M. P.; Jorgensen, W. L. *J. Chem. Phys.* **2002**, *116*, 112–122.

Table 4. Heats of Reaction (kcal/mol)^a

		exptl ^b	MP2(full)	MP2	B3LYP
1 0	Ph ₃ As=S + Ph ₃ P → Ph ₃ As + Ph ₃ P=S	-17.7 ± 0.8	-18.3	-16.9	-16.3
1 1	Ph ₃ P=S + Me ₃ P → Ph ₃ P + Me ₃ P=S	-5.6 ± 0.5 ^c	-1.3	-1.5	-5.1
1 2	Ph ₃ As=S + Me ₃ As → Ph ₃ As + Me ₃ As=S		1.2	1.0	-1.1

^a All energy calculations at the MP2 geometry using 6-31+G(d) for S, 6-31G(d) for As and P, and 6-31G for C and H with ZPE included. All values are calculated for 0 K. All energies calculated with G3Large for As, P, and S and 6-31(d) for C and H. ^b Derived from ref 15. ^c Based on the square root of the sum of the square of reported errors.

errors are known, such as relativistic effects, inner-shell correlation, and vibrational anharmonicity, by far the largest is the result of the core polarization.⁴⁰ These data suggest that, regardless of the method, basis sets containing tight d functions on the atoms E and Y in molecules of the form R₃E=Y is a prudent approach to doing further calculations.

In the case of rigorously isodesmic reactions, cancellation of most of the error because of the lack of core polarization may be counted on. However, in the instance of R₃P=S and R₃As=S, we did not feel that sufficiently reliable data existed to take this approach. Furthermore, with the goal of determining the energies of reactions, such as eq 5, which are not isodesmic at all, in addition to determining the P=S and As=S bond strengths, it is clear that core polarization had to be used.

Among nonspecialists,⁴⁸ the Gn methods, represented most recently by G3, have become standard methods for thermochemical calculations of molecules of modest size because of their relatively good accuracy and ease of use, particularly within the commercial suite of quantum chemistry programs known as GaussianXX (with XX implying the year of the update). These methods are born of the idea that a high-level calculation with a large basis set can be well-approximated by several smaller calculations that generate “corrections” to a calculation using that same level of theory with smaller basis sets. (An additional, empirically derived, correction is also added to generate the best possible thermochemical data.) One of the key differences between the G2 and G3 methods is the inclusion of core polarization in the new “G3Large” basis set. Thus, although all the Gn methods, including G3, still have some difficulty with the oxides of P and S, and thus, we *assume* for all the R₃E=S and R₃E=O compounds, it is rational to believe that this error is minimized by using the G3 method, compared to others. Furthermore, because of the systematic nature of the errors, we can further assume (1) that the errors will approximately cancel out in isodesmic and quasi-isodesmic reactions and (2) that the stability of that compound is underestimated by 2–5 kcal/mol because of that particular functionality in nonisodesmic reactions involving a R₃E=Y species. Because the experimental data are very limited, we

Table 5. P=S and As=S Bond Strengths (kcal/mol)

	exptl ^a	G3	best estimate ^b
H ₃ P=S		61.7	63.7
H ₃ As=S		46.3	48.3
Me ₃ P=S	94	85.5	87.5
Me ₃ As=S		67.5	69.5
Ph ₃ P=S	88		82.4
Ph ₃ As=S	70		68.4

^a From ref 15. Stated uncertainties are 3 kcal/mol. ^b For the H and Me derivatives, these values are taken from the G3 estimates with 2 kcal/mol added to compensate for the shortcomings in those calculations. For the Ph derivatives, the value is derived from the Me derivative and the isodesmic reactions in Table 4. See text for a full explanation.

are forced to use this speculative extension; future work may show that the systematic error of G3 is not as consistent throughout this series as might have been guessed from the currently available data.

To estimate data for the triphenyl derivatives, the strategy employed was to use G3 calculations on small molecules and isodesmic ligand-exchange reactions between triphenyl and trimethyl or trihydrido derivatives calculated at a lower level of theory. The MP2 and B3LYP methods, with appropriate basis sets, were tested to discern which of them was most consistent with G3. The G3Large basis set was used to include core polarization, as opposed to the cc-pV-(n+d)Z basis sets of Dunning,^{49,50} for consistency and because the latter are considerably larger.

R₃E=Y Bond Strengths. The R₃E=Y values that can be obtained from the present G3 calculations are shown in Table 5. The calculated P=S bond strength in Me₃P=S has been reported⁵¹ using a variation on the G3 method called G3//B3LYP,⁵² in which B3LYP-based geometries are used instead of MP2(full)-based geometries. (This method is reported to give a slightly smaller error in the heat of formation of SO₂ and related compounds.⁵²) The reported G3//B3LYP value is 85.1 kcal/mol,⁵¹ which is not significantly different than the value reported here, but both vary from the experimental estimate of 94 kcal/mol.¹⁵

It is notable that the calculated E=S bond energies are much different for H₃E and Me₃E. Similar phenomena are characteristic of sulfoxides and related compounds; thus we

(47) Wilson, A. K.; Dunning, T. H., Jr. *J. Phys. Chem. A* **2004**, *108*, 3129–3133.

(48) We insert the term “nonspecialists” only to imply that developers of computational methods continue to explore a variety of other approaches.

(49) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244–9253.

(50) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548–10560.

(51) Chesnut, D. B.; Quin, L. D. *Heteroat. Chem.* **2004**, *15*, 216–224.

(52) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650–7657.

are not surprised by this result. For example, the transfer of oxygen from Me_2SO to H_2S is endothermic by 22 kcal/mol (G3, 0 K).⁵³ In other examples taken from our earlier work, the calculated stereochemical inversion barriers are much different for H_2SO than for Me_2SO .⁵⁴ Similarly, the energetics of HOS versus HSO radicals are much different than MeSO versus MeOS radicals, as briefly reviewed previously.⁵⁵

To obtain computational estimates for the $\text{E}=\text{Y}$ bond strength in the triphenyl derivatives, we must choose an appropriate set of isodesmic reactions calculated at a lower level of theory. The data in Table 5 indicate that the bond strength for $\text{H}_3\text{E}=\text{S}$ is more than 20 kcal/mol weaker than that of $\text{Me}_3\text{E}=\text{S}$, whereas the results of Capps suggested that the difference of Ph versus Me should only be on the order of 6 kcal/mol. Furthermore, there is considerably more variability in the results shown in Table 2 for the reactions that involve the hydrides than there is for those involving the methyl derivatives. Between this and the experiences alluded to previously, it was decided to use the methyl derivatives, rather than the hydrides as the basis for isodesmic reactions.⁵⁶

We now consider which of the other methods best matched the G3 calculations. The G2 calculations, which are actually somewhat *more* expensive than G3 and are thus not practical either, merit a short discussion. It is, in all likelihood, no coincidence that reactions 4, 5, 7, and 8, as written, are all slightly less exothermic at G2 than at G3. Because of the lack of core polarization in G2, the stability of the $\text{Me}_3\text{As}=\text{S}$ and $\text{Me}_3\text{P}=\text{S}$ is probably underestimated in a systematically greater manner than any of the other compounds, as is understood for SO_2 , sulfoxides, etc.

In principle, there should be no advantage to MP2 calculations with frozen cores (designated MP2) over MP2-(full) calculations because the correlation energy below the valence shells should also be recovered in the latter. The inclusion of core polarization functions in the G3Large basis set is also more consistent with the use of MP2(full) calculations. There does not seem to be a systematic variation between MP2 and MP2(full), and thus, we choose the MP2-(full) data over the MP2 data with frozen cores for these fundamental reasons.

The empirical conclusion, when comparing the MP2(full) and B3LYP results in Table 2 to the G3 values for eqs 2–5 and 6–9, depends on which data one examines. For the full data set, the average absolute deviation is slightly lower for MP2 than B3LYP (0.9 vs 1.2 kcal/mol). However, when only the reactions involving Me_3E and $\text{Me}_3\text{E}=\text{S}$ are considered, the deviation trend is in favor of B3LYP (0.45 vs 0.9 kcal/mol), and the B3LYP numbers are not systematically in one

Table 6. Enthalpies for Sulfur Atom Transfer from Propene to R_3E (kcal/mol)

		G3	Best estimate ^a
8		-24.6	-26.6
5		-6.2	-8.2
13			-21.5
14			-7.1

^a G3 values are adjusted by 2 kcal/mol to compensate for the underestimation of stability of $\text{R}_3\text{E}=\text{S}$. Values for eqs 13–14 are determined from the best estimates for eqs 8 and 5 plus the isodesmic-exchange reactions 11 and 12.

direction or another. Finally, there is better agreement for eq 11 between experiment and B3LYP than between experiment and MP2. The Hoff group directly measured the enthalpy of reaction 10,¹⁵ but that reaction does not provide a basis for choice between the methods. We thus conclude that, at least on an empirical basis for this data set, the B3LYP numbers are a better choice.

Thus, we arrive at determining the “best-estimate” values listed in Table 5. For $\text{H}_3\text{P}=\text{S}$, $\text{H}_3\text{As}=\text{S}$, $\text{Me}_3\text{P}=\text{S}$, and $\text{Me}_3\text{As}=\text{S}$, these are the G3 calculations, with an extra 2 kcal/mol added to compensate empirically for the assumption that, like $\text{R}_3\text{P}=\text{O}$, SO_2 , SO_3 , and R_2SO , G3 underestimates the stability of the sulfides by a few kcal/mol. The choice of 2 kcal/mol is arbitrary, but is on the conservative side and sits well within the range observed for the other compounds.

The values for $\text{Ph}_3\text{P}=\text{S}$ and $\text{Ph}_3\text{As}=\text{S}$ are obtained from the best-estimate values from Table 5 for the methyl compounds and the B3LYP values for the isodesmic exchange of Ph for Me from Table 4. While the agreement between these predictions and the experimental estimate for $\text{Ph}_3\text{As}=\text{S}$ is good, that for $\text{Ph}_3\text{P}=\text{S}$ is disappointing, in that our computational estimate is almost 6 kcal/mol lower.⁵⁷ Some of that could be artificially recovered by using the MP2(full) isodesmic-reaction energy from Table 4, instead of the B3LYP reaction energy. However, there does not seem to be any justification for that, particularly in that the G3 estimate for Me_3P is also much lower than the experimental estimate. Moreover, the authors of the experimental paper note¹⁵ that they estimate a $\text{P}=\text{S}$ bond strength for $\text{Bu}_3\text{P}=\text{S}$ that is 4 kcal/mol higher than a previous report and suggest that a middle-ground value ought to be taken as the best experimental estimate.

Enthalpies of S Atom Transfer from Alkenes to R_3E . Calculated energies for S atom transfer from alkenes to phosphines and arsines are given in Table 6. The approach here is analogous to that above; we take the G3 values from Table 2, adjust them by 2 kcal/mol to compensate for the underestimation of $\text{Me}_3\text{E}=\text{S}$ stability, and then use the B3LYP isodesmic reactions from Table 4 to bring in the phenyl derivatives. The choice of propene as the model olefin

(53) Me_2SO –552.93575, Me_2S –477.770476, H_2SO –474.368709, H_2S –399.238376 in Hartrees.

(54) Cabbage, J. W.; Jenks, W. S. *J. Phys. Chem. A* **2001**, *105*, 10588–10595.

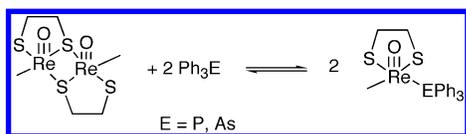
(55) Gregory, D. D.; Jenks, W. S. *J. Org. Chem.* **1998**, *63*, 3859–3865.

(56) Also, the reactions would be closer to rigorously isodesmic with methyl derivatives than with hydrides.

(57) It should be noted that ours are 0 K gas-phase results, not condensed-phase results in benzene.

is arbitrary (but seemed more representative than ethylene), and an adjustment could be made to any other olefin by a straightforward isodesmic-exchange reaction of the corresponding alkenes and thiiranes. The clear conclusion to be drawn from Table 6 is that while the S transfer from thiiranes to phosphines is clearly more exothermic, the transfer to arsines is also thermodynamically reasonable and ought to go to completion in most cases.

The experimental results indicate that this is so.^{14,58} The relative rates of the reactions, however, derive from side reactions involving the catalysts. For example, atom-transfer reactions using the illustrated dimeric catalyst are about 10² times more rapid using the illustrated dimeric catalyst than when using its monomeric analogue, all other conditions being equal. Moreover, the rate of atom-transfer reactions with the superior dimeric catalysts (considering Ph₃P relative to Ph₃As as receptors) is Ph₃As ≫ Ph₃P because the side reaction of catalyst monomerization, which leads to the great lessening of catalytic activity, occurs only for the former ligand. Ph₃As is too weak a Lewis base to drive the catalyst-deactivating monomerization to an appreciable extent.



Bonding in R₃E=S. Two recent treatments of the bonding in compounds such as trimethylphosphine sulfide and trimethylarsine sulfide merit some discussion in the context of this work. Dobado and co-workers applied Bader's "Atoms in Molecules" method to describe the bonding in the oxides of amines, phosphines, and arsines.⁵ An advantage of this approach is that it does not depend on the method of bond localization used or the basis set chosen, but rather, it is based on the total electron density and the characters of local minima and maxima to describe bonding.⁵⁹ Dobado was interested in distinguishing between models that advocated (i) a σ bond and two π bonds, (ii) a σ bond and three back-bonds, and (iii) three banana bonds. The AIM analysis showed a bond critical point along the σ bond axis and three more trigonally disposed about the O (or S) atom in an arrangement that supports the notion of a highly polarized σ bond and three lone pairs on O (or S) in an orientation staggered with respect to the substituents on the central element (E). The degree of ionicity of the σ bond depended on the difference in electronegativity between E and O (or S). They conclude that "the XZ bond in the Y₃XZ series of molecules is a single, highly polarized σ bond, with strength dependent on the electrostatic interactions between the X and Z atoms."⁵

Chesnut and co-workers used a different analysis, also based on AIM, but used delocalization indices and a par-

Table 7. Mulliken Charges and Bond Orders for R₃E=S

	charge, E	charge, S	bond order
Me ₃ P=S	0.78	-0.50	1.55
Me ₃ As=S	0.50	-0.46	1.42
Ph ₃ P=S	0.87	-0.51	1.52
Ph ₃ As=S	0.40	-0.47	1.38

ticular description of bond order based on the Cioslowski–Mixon bond localization scheme.¹⁰ By this method, the ionic contribution to the total bond P–S (or P–O) bond order for Me₃P=S (or =O) is 36% or 43%, respectively. They state that the ionicity of the P–O bond is about 67%, whereas that of the P–S bond is about 4%.

It is not reasonable to give quantitative comparisons of quantities, such as bond order, atomic charge, ionicity, and the like, unless precisely the same calculations are done across a series of compounds. Although each system is sensible in its own way, the definitions are different (some might say arbitrary), and some systems end up being sensitive to basis set. Thus, in this paper, we do not attempt to quantitatively add the arsine sulfides to the table of values reported by Chesnut.

Since the main value of the calculated bond orders resides in their relative values in a series rather than their absolute values, we feel comfortable commenting briefly on the simple Mulliken charges and bond orders obtained here, and presented in Table 7. These were obtained with only 6-31G(d) basis sets for P and S and 6-31G basis sets for As, P, and S, and 6-31G basis sets on C and H; this is known to be a basis set where the Mulliken scheme performs well.⁶⁰ Comparable S=O bond indices are about 1.36 for simple dialkyl sulfoxides and about 1.60 for simple sulfones.^{61,62}

Both charge separation and bond order are somewhat higher for the phosphine sulfides, compared to that of the arsine sulfides. This is not simply a matter of electronegativity, since the electronegativity of P and As are nearly identical. We speculate that the more chemically reasonable rationalization is that overlap between two second-row elemental atomic orbitals is better than between a second and a third row element. (This phenomenon is widely recognized, if not well documented, in comparison of first row–first row bonds to first row–second row bonds.) Better overlap in a dative σ bond should result in greater electron donation from P to S than from As to S and thus a greater charge separation. To partially compensate for this greater charge separation, the electron density associated with the nonbonding electrons, formally based on the sulfur, will be polarized back toward the P nucleus, which will again increase the strength of the interaction.

To avoid semantic issues deriving from the method of localization, it is preferable and straightforward to look at the canonical orbitals for such a distortion. These orbitals are symmetry adapted, though, and thus have a

(58) Ibdah, A.; Jenks, W. S.; Espenson James, H. **2005**, manuscript in preparation.

(59) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990.

(60) Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* **1993**, *14*, 1504–1518.

(61) Cabbage, J. W.; Vos, B. W.; Jenks, W. S. *J. Am. Chem. Soc.* **2000**, *122*, 4968–4971.

(62) Cabbage, J. W.; Guo, Y.; McCulla, R. D.; Jenks, W. S. *J. Org. Chem.* **2001**, *66*, 8722–8736.

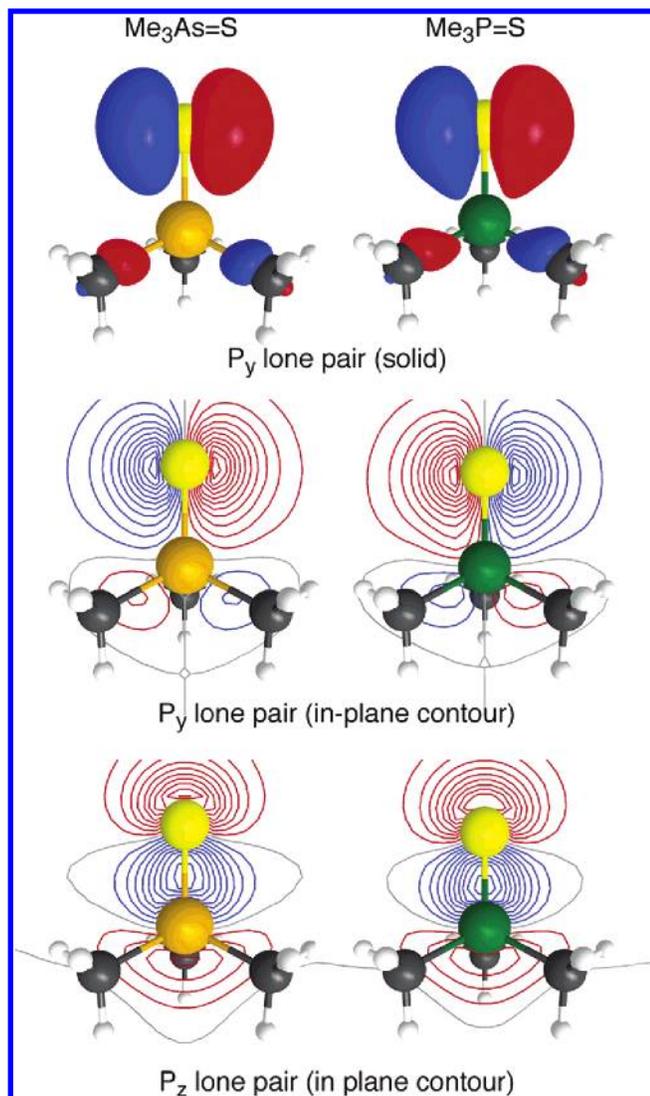


Figure 1. Nominally nonbonding orbitals in $\text{Me}_3\text{As}=\text{S}$ (orange central atom) and $\text{Me}_3\text{P}=\text{S}$ (green central atom).

different look than the localized ones most often considered. Illustrated schematically below, the three approximately nonbonding pairs derive from an sp_z hybrid pointing along the E–S axis away from E (gray) and from the two p_x and p_y valence orbitals (blue and green, respectively) on S. A localized picture of nonbonding pairs would have three equivalent banana bonds or three sp^3 -like hybrid nonbonding orbitals.

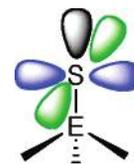


Figure 1 illustrates the sp -type nonbonding pair and the p_x -based orbital, which is degenerate with the (not illustrated) p_y -based pair as a pair of HOMOs. The p_y -based orbital is essentially identical, save that it interacts mainly with the single methyl group in the center of the drawing, rather than the outer two. The solid drawings are cut off at the 0.95 contour, and the contour plots (in the plane of the page) are shown below. Clearly, there is greater distortion of the orbital and thus “back-bonding” or electrostatic attraction for the phosphine sulfide than for the arsine sulfide. The sp -type lone pair, illustrated as contour plots through the plane of the paper, is the next orbital down and clearly has some bonding character. However, the corresponding orbitals in the two compounds are much more similar.

Conclusions

The computed values of 82 and 68 kcal/mol for the E=S bond strengths of $\text{Ph}_3\text{P}=\text{S}$ and $\text{Ph}_3\text{As}=\text{S}$ are certainly subject to some uncertainty. The two major sources are the reliability of the G3 method for sulfides of this type, given its overestimation of total energies for related oxides, and a surprisingly large difference in the enthalpy of an isodesmic-exchange reaction between $\text{Me}_3\text{P}=\text{S}$ and Ph_3P calculated using B3LYP and MP2(full) methods. Nonetheless, these data confirm that the experimental estimates of 88 ± 3 and 70 ± 3 kcal/mol, respectively, are reasonable. Further refinement will require additional experimental work and an enhanced ability to treat molecules of this size with computations of sufficiently accurate computational models. It is clear, however, that S atom transfer from thiiranes to arsines and phosphines is exothermic.

Acknowledgment. The authors gratefully acknowledge support from Iowa State University and NSF (CHE 0213375).

Supporting Information Available: Cartesian Coordinates and absolute energies of all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC051228W