

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228860819>

Toward an expanded oxygen atom transfer reactivity scale: Computational investigation of the energetics of oxo transfer reaction couples

ARTICLE *in* INORGANICA CHIMICA ACTA · DECEMBER 2007

Impact Factor: 2.05 · DOI: 10.1016/j.ica.2007.10.047

CITATIONS

17

READS

9

2 AUTHORS, INCLUDING:



R. H. Holm

Harvard University

338 PUBLICATIONS 16,640 CITATIONS

SEE PROFILE

Toward an expanded oxygen atom transfer reactivity scale: Computational investigation of the energetics of oxo transfer reaction couples

Sonny C. Lee ^{a,*}, R.H. Holm ^{b,*}

^a Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

^b Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA

Received 1 October 2007; accepted 28 October 2007

Available online 6 November 2007

Dedicated to Professor Edward Solomon, whose research achievements in inorganic and bioinorganic optical spectroscopy and theory are unsurpassed in their elegance, scope, and impact.

Abstract

The computational prediction of gas phase enthalpy (neutral substrates) and aqueous free energy (anion substrates) changes has been evaluated for the oxygen atom transfer reaction $X + 1/2O_2 \rightarrow XO$. Several density functionals (SVWN, BP86, B3LYP) at double- and triple- ζ levels were surveyed, along with one composite ab initio method (G3(MP2)). Results are presented for extensive main group test sets for which experimental thermochemistry is available. In addition, several minimal reaction couples of the type $[M^{IV}OL_2]/[M^{VI}O_2L_2]$ ($M = Mo, W$) have been examined. Overall, the results suggest a computational approach to the energetics of oxo transfer is feasible, potentially affording an expanded oxo transfer reactivity scale.

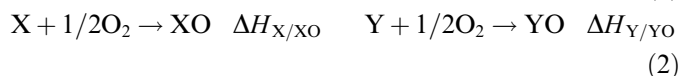
© 2007 Elsevier B.V. All rights reserved.

Keywords: Oxygen atom transfer reactions; Density functional theory (DFT); Thermochemistry

1. Introduction

We have previously introduced a thermodynamic reactivity scale for the generalized oxygen atom (oxo) transfer reaction (1) [1,2]. Reactions of interest here are *primary* oxo transfer reactions in which XO/X and YO/Y are oxygen atom donors/acceptors, and the oxidation state changes by two units as a result of atom transfer only. The essential thermochemical aspects of the reactivity scale have been described [2]. Reaction (1) is the formalized sum of reaction couples (2) taken in the appropriate direction. Reaction (1) proceeds spontaneously if $|T\Delta S| \ll |\Delta H|$ and $\Delta H_{X/XO} > \Delta H_{Y/YO}$. The treatment leads to the gas-phase bond dissociation energy D of an oxidized molecule XO

from Eq. (3), in which $\Delta_f H_m^0 = 59.55$ kcal/mol for the process $1/2O_{2(g)} \rightleftharpoons O_{(g)}$



Atom transfer couples (2) are conceptually simple reactions that summarize fundamental thermochemical relationships and form the basis of the reactivity scale. These couples can be used to predict reaction direction and bond strengths, and find application *inter alia* in synthetic methods, catalysis, and bioinorganic chemistry. When the couples are arranged in an order of decreasing ΔH , a reactivity series emerges. Thus, the reduced member Y of a couple Y/YO with a smaller (more negative) ΔH is thermodynamically competent to reduce the oxidized member

* Corresponding authors.

E-mail addresses: sclee@uwaterloo.ca (S.C. Lee), holm@chemistry.harvard.edu (R.H. Holm).

of a couple X/XO with a larger ΔH . Several compilations of reaction couple enthalpies are available, the most extensive of which was published in 1993 [2]. Additional values can be calculated from currently available standard heats of formation, values of which are available through various Internet sources such as the NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>). These values are primarily those of light main group (2p and, to a lesser extent, 3p) compounds. Reliable thermochemical data are sparse for compounds of the heavier main group elements and the transition elements.

Modern quantum chemical methods, in conjunction with steady advances in computational performance, provide one promising means to fill gaps and expand otherwise experimentally derived tabulations of reaction couple enthalpies. To trust computationally predicted relative molecular energies as chemically meaningful for unknown oxo transfer reaction couples, it is essential to assess the accuracy of test calculations against existing data across a sufficient range of species of interest. We present such an analysis here, with the following specific goals: (i) to calibrate various quantum chemical methods as applied to the thermochemistry of oxo transfer; (ii) to gauge reliability as a function of computational model chemistry and compound type; and (iii) to extend the calculations to species where experimental and thermochemical data are unavailable.

In principle, both thermochemical and computational methodology can be applied to any atom or group transfer reaction. The primary emphasis in these laboratories has been on oxo transfer because of the occurrence of such reactions in molybdenum and tungsten enzymes and their synthetic analogue reaction systems [3–5]. Oxygenation reaction energies have been evaluated as computational benchmarks in at least one previous instance, although the reactions chosen were unrestricted with respect to reaction type [6]. We also note the recent formulation of a thermodynamic reactivity scale for sulfur atom transfer based on experimental thermochemical data [7].

2. Computational methodology

For the experimentalist interested in calculating oxo transfer energetics, a useful quantum chemical approach should apply broadly to all potential species of interest, provide chemically useful (or best possible) relative energies, employ standard (unmodified) methods and basis sets, and avoid excessive computational demands. For our experimentally defined test set, prototype compounds were chosen to span the main group (2p–5p) elements, including both neutral and anionic species, with the inclusion of select isostructural molybdenum and tungsten complexes. The need to analyze heavy element compounds, particularly transition metal complexes where experimental thermochemical data are conspicuously lacking, requires satisfactory treatment of electron correlation at reasonable computational cost; this effectively restricts the choice of

method to some form of density functional theory (DFT) [8].

Two popular DFT approaches were chosen for detailed consideration using triple- ζ level basis sets. In the first treatment, the combination of the B3LYP hybrid density functional [9] and 6-311+G(2d,p) triple- ζ split valence basis set [10] was investigated via the GAUSSIAN 03 (G03) program [11]. Inasmuch as no triple- ζ , all-electron bases internal to the G03 package include elements beyond krypton [12], the 6-311+G(2d,p) basis set was supplemented, for heavier elements, with the relativistically corrected, double- ζ , effective core potential (ECP) LANL2DZ basis [13]; we designate this mixed basis set as 6-311ECP where relevant. The desirability of a uniform, all-electron, triple- ζ basis set applicable to all elements of interest prompted the application of a second computational model chemistry using the Amsterdam Density Functional (ADF 2004.01) package [14]. In this instance, the BP86 general gradient approximation (GGA) functional [15] was coupled with the ADF-specific, all-electron TZ2P basis set [16], which is constructed from triple- ζ quality Slater-type orbitals (STO) with two polarization functions; scalar relativistic (ZORA) corrections [17] were applied.

In addition to these general DFT approaches, a third DFT model chemistry, applicable to elements up to xenon, was explored using G03. This approach uses the classic SVWN local density approximation (LDA) functional (Slater exchange and VWN correlation functional III) [18] with the polarized, double- ζ DGDZVP basis set [19], which was developed and optimized specifically with the SVWN functional. The deficiencies of LDA functionals are well-known [8] and they have fallen into disfavor for molecular applications. However, we have found that this unconventional functional/basis set combination yields excellent structural agreement for the optimized geometry of certain metal complexes (*vide infra*), prompting us to assess its thermochemical accuracy as well.

Finally, a GAUSSIAN-3 (G3) composite *ab initio* model chemistry was used to typify the various methods [20] developed expressly for the computation of high accuracy thermochemical data. The G3(MP2) variant [21], which utilizes a combination of Hartree–Fock (HF), second order Møller–Plesset (MP2), and quadratic configuration interaction (QCISD(T)) calculations at various basis set levels, was chosen based on accuracy (mean absolute energy deviation of <1.3 kcal/mol for an extensive test set of light (2p, 3p) element molecules), its extension to lower main group (4p) species [22], and computational economy. While the basis sets and methods used in this and other high accuracy compound approaches confine these protocols to small, light element (typically, 3p and above) species, they are potentially valuable in evaluating oxo transfer couples for main group species at modern computational limits.

All species were constrained to highest possible symmetries whenever feasible and optimized to structural minima, as verified by the frequency calculations that also provided the thermochemical data. Default convergence criteria

were used in all G03 calculations. For ADF calculations, the integration accuracies for geometry optimizations and numerical frequency calculations were set to 6 (i.e., evaluation to 6 significant digits); for species with problematic low frequency modes (some metal complexes and oxyacids), the gradient and coordinate uncertainty criteria for geometry optimization were tightened to as little as 10^{-4} Hartree/Å and 10^{-3} Å, respectively, and integration accuracy increased to 8 for frequency calculations, as needed. To enable comparison with experimental data, aqueous solvent effects were incorporated in all anion calculations via the conductor polarizable continuum model (CPCM) [23] in G03 and the conductor-like screening model (COSMO) [24] in ADF. Standard values for the dielectric constant of water (78.39) and solvent molecule radius (1.385 Å in CPCM, 1.93 Å in COSMO) were used. The PBE0/6-31G(d)-optimized UAKS United Atom Topological Model [25] was used for atomic radii in the CPCM calculations; for COSMO calculations, the optimized radii of Klamt et al. [26] were employed where available, otherwise, the van der Waals radii of Bondi [27], scaled by a factor of 1.2 [26], were used. All reaction energies (enthalpies or free energies) were adjusted to standard thermochemical reference states (298.15 K, 1 atm for gas phase data, 1 M for solution phase data) [10a,28].

3. Results and discussion

Various oxo transfer reaction couples represented by reaction (2) have been computationally examined. These test sets of practical and notional reaction couples are largely drawn from the extensive 1993 compilation of thermochemical data [2]. They span a broad range of energies (*ca.* 135 kcal/mol), and include nearly all substrates associated with the oxotransferase activity of molybdenum and tungsten enzymes. Inasmuch as a primary goal of the present study is computational validation, almost all couples presented in this work have experimental energies, typically accurate to within ± 3 kcal/mol, for comparison; the few cases where experimental data are unavailable are noted explicitly. Our analysis is presented in separate sections that describe neutral couples, divided into 2p and heavier element main group species, anionic couples, and neutral molybdenum and tungsten couples. For neutral molecules, gas phase enthalpies are presented, while aqueous free energies are calculated for ionic species. For the investigation of specific reaction couples, well-chosen isodesmic (bond-type conserving) relationships (e.g., via reaction (1)) are expected to yield more accurate computational reaction energies due to the cancellation of systematic errors [10a,28]. As a general protocol, however, this approach is inapplicable here because our reaction couple comparisons involve oxygen atom addition to a diversity of bonding environments. All enthalpies and free energies were therefore computed directly via the oxygenation reaction (2).

We note that computations using reaction (1) can be coupled with a fixed experimental benchmark for reaction

(2) to create an isogyric (electron-spin conserving) analysis [10a,28], as illustrated in reactions (4) and (5) where the dihydrogen/water couple provides the experimental reference point. The net effect of this isogyric scheme is the introduction of a fixed correction to the reaction energies calculated via reaction (2), the exact value of which depends on the choice of the reference reaction and is equal to the energy of that chosen reference. In theory, an isogyric approach offsets errors in the treatment of electron correlation; in practice, this improves computed energies for those reaction couples most similar in bonding changes to the reference couple, but the effect on more divergent couples is unpredictable



3.1. Neutral 2p couples

Experimental and calculated enthalpies of oxygenation $\Delta H_{\text{X/XO}}$ for 15 neutral 2p substrates are listed, along with deviations of individual calculated results from experimental values and mean average deviations (MAD), in Table 1. Subsequent tables of oxo transfer energetics follow a similar format. As expected, the LDA SVWN method gave the poorest results, with sizable errors (12.6 kcal/mol MAD); the calculated enthalpies are systematically more negative than experiment, which could reflect the known overbinding tendencies of LDA calculations [8]. The GGA BP86 and hybrid B3LYP treatments at triple- ζ basis set levels exhibit comparable performance, with MADs (6.3 and 5.8 kcal/mol, respectively) roughly half that of the SVWN approach. The G3(MP2) model chemistry yielded the best agreement, with a MAD (2.7 kcal/mol) half those of the BP86 and B3LYP results.

Of the couples in this light atom test set, two distinct outlier groups deviate from experiment for all computational methods. Most prominent is the MeNC/MeNCO couple, where a consistent, substantial deviation exceeding 18 kcal/mol is evident. The enthalpy for this couple, unlike all others in this set, derives from liquid phase measurements. While this will introduce error when compared against our gas phase calculations, we estimate the deviation due to solvation and change of state effects at less than 5 kcal/mol by comparison of gas phase vs. liquid phase data for other reaction couples. We have no reason to believe that either isocyanides or isocyanates are in any way problematic from a theoretical standpoint, raising the possibility that the experimental measurement is in error in this case. The second outlier is associated with the amine-*N*-oxides, which, assuming correct experimental thermochemistry, appear to be computationally overstabilized relative to other species in this set. If these outliers are removed from the error analysis, the MADs improve to 12.1, 4.7, 3.8, and 0.5 kcal/mol for the SVWN, BP86, B3LYP, and G3(MP2) results, respectively.

Table 1

Experimental and calculated gas phase enthalpies (kcal/mol, 298.15 K, 1 atm) for oxo transfer reaction couples involving 2p elements in neutral molecules

X	XO	Experiment ^a	SVWN/DGDZVP		BP86/TZ2P		B3LYP/6-311+G(2d,p)		G3(MP2)	
		ΔH	ΔH	Deviation ^b	ΔH	Deviation ^b	ΔH	Deviation ^b	ΔH	Deviation ^b
O ₂	O ₃	34.1	18.9	15.2	31.9	2.2	45.5	−11.4	33.4	0.7
H ₂ O	H ₂ O ₂	25.2	16.4	8.8	24.9	0.3	26.6	−1.4	25.6	−0.4
N ₂	N ₂ O	19.6	−7.5	27.1	7.0	12.6	18.1	1.5	19.1	0.5
Me ₃ N	Me ₃ NO	−2.0 ^c	−3.7	1.7	7.7	−9.7	8.5	−10.5	2.5	−4.5
py ^d	pyO ^d	−12.6	−20.0	7.4	−6.7	−5.9	−1.8	−10.8	−3.8	−8.8
N ₂ O ₃	N ₂ O ₄	−17.8	−41.3	23.5	−24.9	7.1	−17.9	0.1	−18.4	0.6
C ₂ H ₄	c-C ₂ H ₄ O ^d	−25.1	−38.6	13.5	−23.4	−1.7	−20.0	−5.1	−25.0	−0.1
CH ₄	MeOH	−30.1	−33.4	3.3	−25.7	−4.4	−26.3	−3.8	−30.8	0.7
PhMe	PhCH ₂ OH	−34.6	−39.8	5.2	−29.5	−5.1	−30.4	−4.2	−35.7	1.1
PhEt	PhCH(OH)Me ^e		−44.6		−34.1		−35.2		−41.4	
PhH	PhOH	−42.9	−49.3	6.4	−38.2	−4.7	−37.9	−5.0	−42.8	−0.1
MeNC	MeNCO	−50.0 ^f	−84.6	34.6	−71.2	21.2	−68.0	18.0	−68.2	18.2
H ₂	H ₂ O	−57.8	−55.7	−2.1	−52.0	−5.8	−53.0	−4.8	−57.3	−0.5
HCHO	HCO ₂ H	−64.5	−73.3	8.8	−61.1	−3.4	−60.4	−4.1	−64.5	0.0
CO	CO ₂	−67.6	−86.4	18.8	−72.1	4.5	−67.7	0.1	−68.5	0.9
Mean absolute deviation				12.6		6.3		5.8		2.7

^a Experimental data from Ref. [2].^b Deviation = experiment − theory.^c Ref. [29]; an alternate value of −11 kcal/mol has been estimated based on experimental and theoretical data [30].^d py = pyridine (C₅H₅N), pyO = pyridine-*N*-oxide (C₅H₅NO), *c*-C₂H₄O = ethylene oxide.^e Experimental value not available.^f Liquid phase.

The ethylbenzene/1-phenylethanol couple, for which the experimental thermochemistry is unavailable, has been included in the tabulation because of the activity of ethylbenzene dehydrogenase [31].

3.2. Neutral 3p/4p/5p couples

Evaluation of oxo transfer enthalpies involving 3p/4p/5p elements is hindered by the available thermochemical data, which are limited in number and chemical diversity. The poor representation of compounds containing the heaviest elements (4p and lower) in standard computational thermochemical test sets reflects this situation [22,32]. The fourteen oxo transfer couples in Table 2 were selected for analysis. The majority of these couples involve 3p elements and hypervalent species; 4p and 5p oxidations are represented by three couples and one couple, respectively, and four couples involve non-hypervalent centers only. For computational economy, we compare calculations on A₂Me₆/(Me₃A)₂O couples against the experimental data for A₂Et₆/(Et₃A)₂O (A = Ge, Sn).

The computed heavy element oxo transfer energetics are less accurate than those for light element species. Major deviations, consistent in both magnitude and sign, were observed for the SeCl₂/SeOCl₂ and SOF₂/SO₂F₂ couples in all approaches. Given the limitations in the data set, we are uncertain whether these differences arise from theoretical deficiencies or experimental error. For each calculational method, the MADs using all couples are given in Table 2; in the discussion that follows, however, we exclude these two problematic couples from the analysis and in the calculation of MADs.

G3(MP2) theory again gives the lowest MAD at 4.6 kcal/mol, followed quite closely by the BP86/TZ2P calculations with a MAD of 5.3 kcal/mol. The unexpectedly high MAD in the G3(MP2) set comes entirely from large deviations for its predicted enthalpies of the A₂Me₆/A₂OMe₆ couples (A = Si, Ge); for all other couples in this set, the G3(MP2) method is the clear reference standard for thermochemical accuracy.

Surprisingly, the SVWN/DGDZVP gives better results than B3LYP/6-311+G(2d,p) theory, with a deviation of 7.3 vs. 11.6 kcal/mol. In our test set, the disappointing performance of the B3LYP method seems to be associated with its treatment of hypervalent species. In oxo transfer couples where the heavy atom valence shell expands upon oxidation, B3LYP enthalpies show sizable negative deviations from experiment throughout, while the couples involving strictly non-hypervalent centers have smaller, mostly positive deviations. This pattern occurs in the other methods as well, although the negative deviations are less prominent than those in the B3LYP data. For the SVWN approach, the systematic positive deviation observed in the 2p enthalpies disappears in the heavy element survey. A deeper survey with greater chemical diversity is needed to determine if the aforementioned correlations are real or accidental.

The B3LYP performance can be improved upon inclusion of additional polarization functions to the non-hydrogen element basis sets, as demonstrated in Table 3, which compares the results of calculations using a range of Pople-type double- and triple- ζ split-valence bases. Thus, the smallest absolute deviations for the valence-expanding couples, comparable to the SVWN/DGDZVP and BP86/

Table 2

Experimental and calculated gas phase enthalpies (kcal/mol, 298.15 K, 1 atm) for oxo transfer reaction couples involving 3p/4p/5p elements in neutral molecules

X	XO	Experiment ^a	SVWN/DGDZVP		BP86/TZ2P		B3LYP/6-311ECP ^b		G3(MP2)	
		ΔH	ΔH	Deviation ^c	ΔH	Deviation ^c	ΔH	Deviation ^c	ΔH	Deviation ^c
Cl ₂	Cl ₂ O	19.2	8.3	10.9	17.5	1.7	22.3	−3.1	18.4	0.8
SeCl ₂	SeOCl ₂	1.6	−35.1	36.7	−31.3	32.9	−22.2	23.8	−28.8	30.4
SO ₂	SO ₃	−23.6	−19.2	−4.4	−19.6	−4.0	−11.0	−12.6	−22.2	−1.4
Me ₂ S	Me ₂ SO	−27.1	−23.4	−3.7	−23.7	−3.4	−17.1	−10.0	−26.3	−0.8
SOCl ₂	SO ₂ Cl ₂	−33.3	−25.6	−7.7	−26.2	−7.1	−18.3	−15.0	−34.4	1.1
Me ₃ As	Me ₃ AsO	^d	−33.5		−26.5		−26.8		−35.9	
SCl ₂	SOCl ₂	−44.7	−45.8	1.1	−44.5	−0.2	−36.1	−8.6	−43.4	−1.3
SOF ₂	SO ₂ F ₂	−50.3	−28.6	−21.7	−29.8	−20.5	−22.1	−28.2	−38.8	−11.5
Sn ₂ Me ₆	Sn ₂ OMe ₆	−52.6 ^e	−59.5	6.9	−52.4	−0.2	−71.5	18.9	^f	
Me ₂ SO	Me ₂ SO ₂	−52.7	−44.9	−7.8	−44.7	−8.0	−37.4	−15.3	−51.3	−1.4
Ge ₂ Me ₆	Ge ₂ OMe ₆	−58.0 ^e	−70.6	12.6	−62.9	4.9	−66.5	8.5	−74.2	16.2
PCl ₃	OPCl ₃	−64.9	−57.9	−7.0	−54.7	−10.2	−50.6	−14.3	−64.2	−0.7
Me ₃ P	Me ₃ PO	−79.7	−69.9	−9.8	−66.6	−13.1	−64.6	−15.1	−74.4	−5.3
Si ₂ Me ₆	Si ₂ OMe ₆	−99.0	−107.6	8.6	−104.1	5.1	−104.7	5.7	−115.6	16.6
Mean absolute deviation				10.7		8.6		13.8		7.3

^a Experimental data from Ref. [2].

^b 6-311ECP = mixed basis set of 6-311+G(2d,p) for light elements and LANL2DZ for elements beyond Kr.

^c Deviation = experiment – theory.

^d Experimental value not available.

^e Experimental values are for the ethyl homologues.

^f Method not applicable for elements beyond Kr.

Table 3

Basis set dependence of B3LYP oxo transfer reaction enthalpies (298.15 K, 1 atm) as deviations^a (kcal/mol) from experimental values

X	XO	6-31G(d)	6-31+G(d)	6-31+G(d,p)	6-311+G(d)	6-311+G(2d,p)	6-311+G(2df,2pd)	6-311+G(3df,2p)
Cl ₂	Cl ₂ O	−0.5	−0.2	−0.2	−2.7	−3.1	−2.0	−0.7
SeCl ₂	SeOCl ₂	24.7	30.7	30.9	21.5	23.8	25.8	26.4
SO ₂	SO ₃	−17.5	−19.1	−19.1	−20.8	−12.6	−8.8	−5.8
Me ₂ S	Me ₂ SO	−19.4	−15.9	−15.9	−17.7	−10.0	−7.0	−5.0
SOCl ₂	SO ₂ Cl ₂	−21.1	−21.8	−21.8	−23.5	−15.0	−11.0	−7.1
SCl ₂	SOCl ₂	−17.0	−15.6	−15.6	−16.6	−8.6	−6.8	−5.0
SOF ₂	SO ₂ F ₂	−30.4	−36.3	−36.3	−37.3	−28.2	−23.8	−19.4
Sn ₂ Me ₆	Sn ₂ OMe ₆	15.5	18.0	17.9	18.0	18.9	19.3	18.8
Me ₂ SO	Me ₂ SO ₂	−20.7	−22.7	−22.6	−23.8	−15.3	−12.0	−8.3
Ge ₂ Me ₆	Ge ₂ OMe ₆	6.7	10.9	11.2	6.1	8.5	10.3	9.9
PCl ₃	OPCl ₃	−19.4	−18.9	−18.9	−19.7	−14.3	−11.6	−9.1
Me ₃ P	Me ₃ PO	−21.5	−20.7	−20.5	−21.3	−15.1	−13.0	−11.1
Si ₂ Me ₆	Si ₂ OMe ₆	2.9	2.2	2.3	3.8	5.7	8.6	10.1
Mean absolute deviation		16.7	17.9	17.9	17.9	13.8	12.3	10.5

^a Deviation = experiment – theory; experimental data from Ref. [2].

TZ2P results, come from the 6-311+G(3df,2p) basis set, which has been used elsewhere [32] to benchmark DFT calculations with G2 and G3 test sets, followed by the “balanced” [28] 6-311+G(2df,2pd) basis set, which yields an accuracy intermediate to the 6-311+G(3df,2p) and 6-311+G(2d,p) levels. The use of a single set of polarization functions for heavy atoms, as in the popular 6-31G(d) basis set and its 6-31+G(d) and 6-31+G(d,p) variants, or, at the triple- ζ level, in the 6-311+G(d) set, is inadequate for quantitating oxo transfer thermochemistry. Improvements in the agreement for the hypervalent reaction enthalpies, however, come at the cost of increased deviations for the

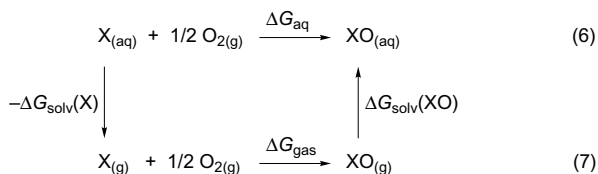
remaining couples. Significant polarization function dependencies have recently been demonstrated for a number of density functionals in the calculated enthalpies of formation for the predominantly 2p element G2/97 test set [32d]. For the B3LYP functional, agreements improved as the size of the polarization set increased. This improvement, however, appears to be fortuitous: B3LYP calculations tend to underbind, skewing deviations in the heats of formation negative, and additional polarization functions simply shift the error distribution in the positive direction. Similar behavior seems to be operative here. The accidental nature of the increased accuracy, coupled

with the added computational cost and the absence of standard basis sets of similar level for elements beyond krypton, limits the utility of these larger basis sets in our study.

We also report in Table 2 calculated enthalpies for the $\text{Me}_3\text{As}/\text{Me}_3\text{AsO}$ couple, which is of interest because of its possible role in the biological detoxification of arsenic. Although the relevant enzyme system has not yet been demonstrated to be a member of the molybdenum/tungsten oxotransferases, the $\text{Me}_3\text{As}/\text{Me}_3\text{AsO}$ couple has been employed in substrate analogues studies of dimethylsulfoxide reductase [33]. While an experimental enthalpy is unavailable for the $\text{Me}_3\text{As}/\text{Me}_3\text{AsO}$ couple, the related couples for $\text{Ph}_3\text{A}/\text{Ph}_3\text{AO}$ ($\text{A} = \text{P}, \text{As}$) are known at -73.8 and -43.1 kcal/mol, respectively [2]. If we assume, from these data points, a constant difference in the phosphine oxide and arsine oxide bond energies of 30.7 kcal/mol and apply this to the experimental $\text{Me}_3\text{P}/\text{Me}_3\text{PO}$ oxygenation enthalpy, we obtain a value of ca. 49 kcal/mol for the $\text{Me}_3\text{As}/\text{Me}_3\text{AsO}$ couple. All methods examined in this work predict a lower enthalpy for this reaction.

3.3. Anion couples

Gas phase oxo transfer couples reflect intrinsic thermochemistry. For neutral molecules, the gas phase data can also be applied directly and satisfactorily in solution phase analyses, as the solvation energies for X and XO are small and therefore (typically) not especially divergent. For ionic species, however, large solvation energies make the consideration of solvent effects essential for meaningful synthetic and biological use. In our DFT calculations, aqueous solution solvation effects were incorporated using ion geometries optimized within a dielectric continuum solvation model (CPCM or COSMO), with the energies subsequently applied to oxo transfer reaction (6). For the G3(MP2) calculations, which are formulated for gas phase thermochemistry, aqueous solvation free energies computed via CPCM at the HF/6-31+G(d)//B3LYP/6-31+G(d) level [34] were used to convert gas phase energies in reaction (7) to aqueous values as in the scheme below [35]. In a recent analysis, the CPCM method has been demonstrated to yield anion solvation energies with MADs of ca. 3–4 kcal/mol [34]. Data are presented in Table 4 as free energies, as is typical for the solution phase thermochemistry of ions.



The anion oxo transfer data set (Table 4) consists mostly of heavy element oxyanions. All species are monoanionic with the exception of the $[\text{AO}_3]^{2-}/[\text{AO}_4]^{2-}$ couples ($\text{A} = \text{S}, \text{Se}$). For protonated oxyanions, the lowest energy hydrogen tautomers and conformers were found within the solvation model by direct computation and relaxed potential energy surface scans. Structures with O–H bonds

were found most stable in all cases except HSO_3^- , where the S–H tautomer (bisulfite) was calculated to be slightly more favorable than the O–H tautomer (sulfonate), in agreement with prior results [36].

The MADs for the aqueous anion couples are slightly greater than for those of the gas phase neutral heavy element species, but do not appear to be significantly worse despite the incorporation of a solvation model in the calculations. The best results were obtained from the G3(MP2) (MAD 6.1 kcal/mol) and BP86/TZ2P (6.3 kcal/mol) approaches, followed by the B3YLP/6-311+G(2d,p) (8.0 kcal/mol), and SVWN/DGDZVP (10.1 kcal/mol) calculations. The couples involving Cl^- , Br^- , and I^- all show large, negative deviations from experiment. We note finally that the small dianions in the test set are not bound in the gas phase [37]. This is of particular concern for G3(MP2) calculations, which provide gas phase results; the energies so obtained are not expected to be meaningful, and this likely explains the large, maximal deviation associated with the $[\text{SO}_3]^{2-}/[\text{SO}_4]^{2-}$ couple.

3.4. Molybdenum/tungsten couples

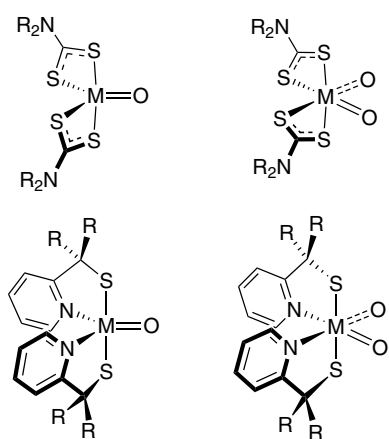
Metal-mediated oxo transfer is a widespread reaction, many examples of which have been organized and summarized elsewhere [1,5,38–40]. The scarcity of experimental thermodynamic data on transition element complexes has hindered the development of an oxo transfer reactivity scale for complexes themselves. Unfortunately, the validation of computational approaches to the evaluation of these couples is also problematic because of this same lack of data. In order to exemplify a quantum chemical approach to the problem, we have chosen two systems for detailed analysis based on the availability of experimental oxo transfer thermochemistry. Both involve well-characterized neutral monooxo Mo^{IV} and dioxo Mo^{VI} species of formulation $[\text{MoO}_n\text{L}_2]$ ($n = 1, 2$), where L is a bidentate, monoanionic ligand, a dithiocarbamate (R_2dtc) in one system [41] and a 2-pyridylmethanethiolate ($\text{L}^{\text{R}}\text{-NS}$) in the other [42], as illustrated in Fig. 1. Molybdenum is a prominent metal in biological oxo transfer reactions [3–5,38]. Given the emergence of tungstoenzymes [3,43,44], we have also calculated the isostructural tungsten complexes for comparison and in anticipation of possible utility in relation to these enzymes. Gas phase models are evaluated against solution phase measurements throughout.

The computationally optimized geometries of the complexes provide a starting point for comparison with experiment. Presented in Table 5 are metal–ligand bond distances of the quantum chemical models compared with those of closely related synthetic species. In general, the calculated structures reproduce the experimental geometries well overall, with metal–ligand bond distances in the DFT structures slightly overlong, for the most part, by 0.03 Å or less. There is one exceptional deviation, however: metal–ligand bond distances affected by the trans influence of oxo ligands are significantly overestimated in typical

Table 4

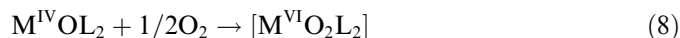
Experimental and calculated aqueous solution free energies (kcal/mol, 298.15 K, 1 M) for oxo transfer reaction couples of anions

X	XO	Experiment ^a	SVWN/DGDZVP		BP86/TZ2P		B3LYP/6-311ECP ^b		G3(MP2)	
		ΔG	ΔG	Deviation ^c	ΔG	Deviation ^c	ΔG	Deviation ^c	ΔG	Deviation ^c
[BrO ₃] [−]	[BrO ₄] [−]	23.8	18.0	5.8	23.8	0.0	29.8	−6.0	18.3	5.5
Cl [−]	[ClO] [−]	22.6	31.3	−8.7	31.7	−9.1	34.2	−11.6	29.8	−7.2
Br [−]	[BrO] [−]	16.9	29.4	−12.5	29.2	−12.3	31.0	−14.1	25.8	−8.9
[IO ₃] [−]	[IO ₄] [−]	16.6	10.2	6.4	15.4	1.2	27.1	−10.5	^d	
[ClO] [−]	[ClO ₂] [−]	12.9	8.9	4.0	8.6	4.3	20.6	−7.7	9.1	3.8
I [−]	[IO] [−]	3.1	22.2	−19.1	19.5	−16.4	23.1	−20.0	^d	
[ClO ₃] [−]	[ClO ₄] [−]	−0.1	6.4	−6.5	6.4	−6.5	17.0	−17.1	3.4	−3.5
[ClO ₂] [−]	[ClO ₃] [−]	−6.0	−9.7	3.7	−10.7	4.7	3.9	−9.9	−12.3	6.3
[HSeO ₃] [−]	[HSeO ₄] [−]	−9.8	−14.7	4.9	−13.2	3.4	−4.9	−4.9	−17.7	7.9
[SeO ₃] ^{2−}	[SeO ₄] ^{2−}	−17.1	−31.2	14.1	−22.1	5.0	−18.1	1.0	−25.5	8.4
[NO ₃] [−]	[NO ₂] [−]	−18.9	−41.5	22.6	−26.5	7.6	−20.5	1.6	−20.8	1.9
[H ₂ AsO ₃] [−]	[H ₂ AsO ₄] [−]	−39.7	−39.5	−0.2	−29.0	−10.7	−31.2	−8.5	−47.2	7.5
[HSO ₃] ^{−c}	[HSO ₄] [−]	−54.5	−59.2	4.7	−43.5	−11.0	−46.3	−8.2	−55.6	1.1
[HCO ₂] [−]	[HCO ₃] [−]	−56.3	−65.4	9.1	−50.5	−5.8	−53.2	−3.1	−59.3	3.0
[SO ₃] ^{2−}	[SO ₄] ^{2−}	−61.7	−82.8	21.1	−60.5	−1.2	−65.3	3.6	−79.7	18.0
[CN] [−]	[OCN] [−]	−64.5	−82.6	18.1	−66.3	1.8	−64.4	−0.1	−66.4	1.9
Mean absolute deviation				10.1		6.3		8.0		6.1

^a Experimental data from Ref. [2].^b 6-311ECP = mixed basis set of 6-311+G(2d,p) for light elements and LANL2DZ for elements beyond Kr.^c Deviation = experiment – theory.^d Method not applicable for elements beyond Kr.^e Sulfonate ([H–SO₃][−]) tautomer; all other H-bearing species (except formate, [HCO₂][−]) are oxyacids.Fig. 1. Schematic representations of $\text{MO}_n(\text{R}_2\text{dtc})_2$ (top) and $\text{MO}_n(\text{L}^{\text{R}}\text{-NS})_2$ (bottom) complexes ($\text{M} = \text{Mo}, \text{W}; n = 1, 2$).

DFT model chemistries (BP86 and B3LYP), with errors that can exceed 0.1 Å. We have also observed this phenomenon in other complexes and with other combinations of DFT method and basis set not reported here [48]. Given the relatively soft, shallow energy surface associated with ligand sites subject to a strong trans influence, the degree of error is perhaps understandable, but we are unaware of previous reports of this behavior. Curiously, the specific combination of the SVWN method and DGDZVP basis set does not suffer from this deficiency, and all primary coordination sphere distances are reasonably well-replicated in this approach, with metal–2p atom bond distances slightly less accurate and metal–sulfur bond distances more

accurate than those from standard DFT treatments; indeed, it is this unexpected accuracy in geometry prediction that prompted the consideration of this unorthodox model chemistry in our thermochemical survey.



Summarized in Table 6 are experimental and calculated enthalpies for the generalized oxo transfer couple 8 ($\text{M} = \text{Mo}, \text{W}$). The experimental enthalpy of the $\text{MoO}(\text{Et}_2\text{dtc})_2/\text{MoO}_2(\text{Et}_2\text{dtc})_2$ couple ($\text{Et}_2\text{dtc} = N,N'$ -diethyldithiocarbamate) has been reported as -35.0 ± 3.2 kcal/mol by direct calorimetry, and -38.2 ± 4.2 kcal/mol by derivation from calorimetrically-defined thermochemical cycles [41]. The computed enthalpies for the Me_2dtc (N,N' -dimethyldithiocarbamate) derivatives bracket these values, with deviations comparable to some of the larger errors observed in the heavy element test set. Somewhat troubling is the discrepancy between the SVWN/DGDZVP and BP86/TZ2P results, which are effectively equivalent to each other, and the B3LYP/6-311ECP calculation, which predicts an enthalpy dramatically higher by ca. 17 kcal/mol; analogous behavior occurs for the $\text{MoO}(\text{L}^{\text{R}}\text{-NS})_2/\text{MoO}_2(\text{L}^{\text{R}}\text{-NS})_2$ couple as well (vide infra). These large differences could be associated with the use of the LANL2DZ ECP basis for molybdenum; discrepancies of similar magnitude also occur in certain instances when the same method/basis set combination was used for tin (Table 2) and iodine (Table 4).

For the $\text{MoO}(\text{L}^{\text{Ar}}\text{-NS})_2/\text{MoO}_2(\text{L}^{\text{Ar}}\text{-NS})_2$ couple ($\text{L}^{\text{Ar}}\text{-NS} = \text{bis}(4\text{-tert-butylphenyl})\text{-2-pyridylmethanethiolate}$), the enthalpy of reaction was estimated to be, at most,

Table 5
Experimental and calculated metal–ligand bond distances (Å) in molybdenum and tungsten complexes

Complex	Bond	Experiment ^a	SVWN/DGDZVP	BP86/TZ2P	B3LYP/6-311ECP ^b
MoO(R ₂ dtc) ₂ ^{c,d}	Mo–O	1.66	1.69	1.68	1.68
	Mo–S	2.41	2.42	2.44	2.48
WO(Me ₂ dtc) ₂	W–O	^e	^f	1.70	1.70
	W–S			2.42	2.45
MoO ₂ (R ₂ dtc) ₂ ^{c,g}	Mo–O	1.70	1.73	1.72	1.72
	Mo–S (trans to oxo)	2.64	2.65	2.71	2.75
	Mo–S (cis to oxo)	2.45	2.44	2.47	2.48
WO ₂ (R ₂ dtc) ₂ ^{h,i}	W–O	1.72	^f	1.73	1.72
	W–S (trans to oxo)	2.66		2.71	2.74
	W–S (cis to oxo)	2.43		2.46	2.48
MoO(L ^R -NS) ₂ ^{j,k}	Mo–O	1.68	1.72	1.70	1.71
	Mo–N	2.17	2.14	2.18	2.21
	Mo–S	2.32	2.32	2.34	2.37
WO(L ^H -NS) ₂	W–O	^e	^f	1.72	1.72
	W–N			2.16	2.18
	W–S			2.33	2.35
MoO ₂ (L ^R -NS) ₂ ^{j,k}	Mo–O	1.70	1.73	1.71	1.72
	Mo–N	2.41	2.39	2.49	2.53
	Mo–S	2.42	2.41	2.44	2.45
WO ₂ (L ^H -NS) ₂	W–O	^e	^f	1.73	1.72
	W–N			2.48	2.49
	W–S			2.44	2.45

^a Experimental metrics are averaged to highest idealized symmetry.

^b 6-311ECP = mixed basis set of 6-311+G(2d,p) for light elements and LANL2DZ for elements beyond Kr.

^c Experimental structure for R = Et; calculated geometries for R = Me.

^d MoO(Et₂dtc)₂, Ref. [45].

^e Experimental structure unavailable.

^f Basis set does not extend beyond Xe.

^g MoO₂(Et₂dtc)₂, Ref. [46].

^h Experimental structure for R = ⁱBu; calculated geometries for R = Me.

ⁱ WO₂(ⁱBu₂dtc)₂, Ref. [47].

^j Experimental structure for R = Ar; calculated geometries for R = H.

^k MoO_n(L^{Ar}-NS)₂ (n = 1, 2), Ref. [42a].

Table 6
Experimental and calculated gas phase enthalpies (kcal/mol, 298.15 K, 1 atm) for oxo transfer reaction couples of molybdenum and tungsten complexes

X	XO	Experiment ΔH	SVWN/DGDZVP ΔH	BP86/TZ2P ΔH	B3LYP/6-311ECP ^a ΔH
MoO(Me ₂ dtc) ₂	MoO ₂ (Me ₂ dtc) ₂	–35.0, –38.2 ^b	–44.8	–45.7	–27.8
WO(Me ₂ dtc) ₂	WO ₂ (Me ₂ dtc) ₂	^c	^d	–62.3	–54.1
MoO(L ^H -NS) ₂	MoO ₂ (L ^H -NS) ₂	< –43 ^c	–51.4	–49.4	–34.9
WO(L ^H -NS) ₂	WO ₂ (L ^H -NS) ₂	^c	^d	–62.6	–58.4

^a 6-311ECP = mixed basis set of 6-311+G(2d,p) for light elements and LANL2DZ for elements beyond Kr.

^b Ref. [41]; experimental enthalpies for diethyldithiocarbamate derivative.

^c Experimental value not available.

^d Basis set does not extend beyond Xe.

^e Ref. [42a]; experimental limiting enthalpy for bis(4-*tert*-butylphenyl)-2-pyridylmethanethiolate derivative.

–43 kcal/mol based on substrate reactivity assays [42a]. This figure is consistent with the results of the SVWN/DGDZVP and BP86/TZ2P calculations on the L^H-NS ligated systems (L^H-NS = 2-pyridylmethanethiolate), which predict enthalpies somewhat below this limit. In the calculations, the ligand was simplified by removal of the sterically shielding *tert*-butyl group; the complexes are

otherwise unperturbed with respect to the primary coordination sphere. The B3LYP/6-311ECP enthalpy, on the other hand, exceeds the experimental upper bound by 8 kcal/mol, and is therefore incorrect with respect to the experimental reference scale. This discrepancy is, however, consistent with the general prevalence of positive deviations in oxo transfer enthalpies observed for this approach;

it is possible that an internal thermodynamic scale constructed entirely from B3LYP/6-311ECP data might be reasonably consistent in ordering and relative quantitative accuracy. An earlier DFT investigation by Thomson and Hall [49] probed the energetics and mechanism of this reaction system using a simplified imine-thiolate ligand representation ($[\text{HN}=\text{CHCH}_2\text{S}]^-$) in place of $\text{L}^{\text{Ar}}\text{-NS}$ and the B3P86 functional at the double- ζ level, with the molybdenum atom described by a modified, double- ζ quality ECP basis; enthalpies for the $\text{MoO}(\text{HN}=\text{CHCH}_2\text{S})_2/\text{MoO}_2(\text{HN}=\text{CHCH}_2\text{S})_2$ and $\text{Me}_3\text{P}/\text{Me}_3\text{PO}$ couples were predicted to be -42 kcal/mol and -61 kcal/mol, respectively. All of the methods surveyed in our work place the $\text{MoO}(\text{L}^{\text{H}}\text{-NS})_2/\text{MoO}_2(\text{L}^{\text{H}}\text{-NS})_2$ couple as more exothermic than the equivalent Me_2dtc reaction system by $4\text{--}7$ kcal/mol; the potential intermetal oxo transfer reaction of $\text{MoO}(\text{L}^{\text{H}}\text{-NS})_2$ with $\text{MoO}_2(\text{Me}_2\text{dtc})_2$ presents an interesting test of this prediction, although its feasibility is uncertain due to the likelihood of oxo-bridge forming side reactions.

Experimental values for the tungsten couples are unavailable. In comparison to the computed molybdenum oxo transfer energetics, the analogous tungsten reactions show the expected increases in exothermicity, although the amounts differ greatly depending on method. This variation appears to originate from the anomalous enthalpies associated with the molybdenum B3LYP/6-311ECP calculations, inasmuch as the equivalent B3LYP/6-311ECP tungsten data are much closer in energy to the BP86/TZ2P predictions. In contrast to the molybdenum data and the B3LYP/6-311ECP result for tungsten, the BP86/TZ2P enthalpies for tungsten are essentially unaffected by ligand type. The more negative values for the tungsten couples relative to molybdenum couples can be ascribed to differences in metal–oxo bond strengths; for example, the W–O bond energy in $[\text{WOCl}_4]$ has been estimated by DFT (BP86 at triple- ζ level) to be 18.6 kcal/mol larger than the Mo–O bond in $[\text{MoOCl}_4]$ [50], which is comparable to the enthalpy differences observed here.

4. Summary and conclusions

This study has examined the feasibility of quantum chemical calculation of quantitative oxo transfer thermodynamics. Four computational model chemistries – three DFT approaches (SVWN at double- ζ level, BP86 and B3LYP at triple- ζ level) and one composite ab initio method (G3(MP2)) – have been evaluated, with performance assessed using reference reaction (2). Because we seek to validate the performance of various computational procedures, the calculations have been restricted in nearly all instances to reactions for which energy data are available. We draw the following principal conclusions.

1. For light (2p) element species, mean absolute errors in calculated gas phase reaction energies decrease in the order $\text{SVWN} > \text{BP86} \geq \text{B3LYP} > \text{G3(MP2)}$. The G3(MP2)

calculations yield clearly superior results overall, as expected for a method specifically constructed to give chemically accurate energies. At the other extreme, the SVWN approach consistently underestimates reaction enthalpies, sometimes substantially, and is not recommended for this application.

2. The ordering of errors changes to $\text{B3LYP} > \text{SVWN} > \text{BP86} > \text{G3(MP2)}$ when oxo transfer involves a heavy (3p/4p/5p) main group element. G3(MP2) theory again yields the best results. Surprisingly, the SVWN method outperforms the B3LYP method, and it is now the B3LYP results that exhibit systematic deviations, in this case overestimating enthalpies.
3. The absolute deviations for solution free energies of anion couples are comparable to the errors in gas phase enthalpies of the heavy element test set, in the order $\text{SVWN} > \text{B3LYP} > \text{BP86} > \text{G3(MP2)}$. The G3(MP2) method, while still the most accurate on average, is no longer the obvious reference standard for computational accuracy.
4. Computed enthalpies for oxo transfer couples involving molybdenum centers are generally consistent, for the most part, with the extremely limited experimental data available. In considering the optimized geometries of these complexes and their tungsten analogues, the SVWN calculations are distinctly adept at replicating trans-influenced bond distances.

The results presented serve as a guide for the calculation of reaction couples with components resembling those in Tables 1–4. The calculated energetics of reaction couples that lack experimental thermochemical definition may be interleaved, at least approximately, with experimental results to produce an expanded reactivity scale. When integrated with reactivity information, metal complexes may be bracketed within the scale, leading to the prediction of thermodynamically allowed metal-mediated substrate transformations. However, accurate placement of metal complexes requires direct thermochemical data or, lacking such information, DFT calculations of reaction couples and a modicum of thermochemistry with which to assess the results.

Acknowledgments

This research was supported by NSF Grant 00547734 at Harvard University and by NSERC at the University of Waterloo. We thank Dr. D.G. Nocera (MIT), Dr. M. Nooijien (Waterloo), and SHARCNET (www.sharcnet.ca) for access to computational resources.

References

- [1] R.H. Holm, *Chem. Rev.* 87 (1987) 1401.
- [2] R.H. Holm, J.P. Donahue, *Polyhedron* 12 (1993) 571.
- [3] J.H. Enemark, C.G. Young, *Adv. Inorg. Chem.* 40 (1994) 1.

- [4] C.G. Young, in: B. Meunier (Ed.), *Biomimetic Chemistry of Molybdenum*, World Scientific Publishing Co., Singapore, 2000, p. 415.
- [5] J.H. Enemark, J.J.A. Cooney, J.-J. Wang, R.H. Holm, *Chem. Rev.* 104 (2004) 1175.
- [6] A.C. Scheiner, J. Baker, J.W. Andzelm, *J. Comput. Chem.* 18 (1997) 775.
- [7] J.P. Donahue, *Chem. Rev.* 106 (2006) 4747.
- [8] W. Koch, M.C. Holthausen, *A Chemist's Guide to Density Functional Theory*, second ed., Wiley-VCH, Weinheim, 2001.
- [9] (a) A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648;
(b) C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785;
(c) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* 157 (1989) 200.
- [10] (a) W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986;
(b) A description of the basis set implementation in G03, with complete references, can be found in Ref. [12].
- [11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P. Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J.Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M. W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *GAUSSIAN 03*, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
- [12] A. Frisch, M.J. Frisch, G.W. Trucks, *GAUSSIAN 03 User's Reference*, Gaussian, Inc, Wallingford CT, 2003. The information is available online at www.gaussian.com.
- [13] (a) P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 270;
(b) W.R. Wadt, P.J. Hay, *J. Chem. Phys.* 82 (1985) 284;
(c) P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 299.
- [14] ADF2006.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <<http://www.scm.com>>;
(b) G. te Velde, F.M. Bickelhaupt, S.J.A. van Gisbergen, C. Fonseca Guerra, E.J. Baerends, J.G. Snijders, T. Ziegler, *J. Comput. Chem.* 22 (2001) 931;
(c) C. Fonseca Guerra, J.G. Snijders, G. te Velde, E.J. Baerends, *Theor. Chem. Acc.* 99 (1998) 391.
- [15] (a) A.D. Becke, *Phys. Rev. A* 38 (1988) 3098;
(b) J.P. Perdew, *Phys. Rev. B* 33 (1986) 8822; Erratum:(c) J.P. Perdew, *Phys. Rev. B* 34 (1986) 7406; The BP86 GGA correction is applied to the VWN (functional V) LDA functional:(d) S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [16] E. van Lenthe, E.J. Baerends, *J. Comput. Chem.* 24 (2003) 1142.
- [17] (a) E. van Lenthe, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.* 99 (1993) 4597;
(b) E. van Lenthe, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.* 101 (1994) 9783;
(c) E. van Lenthe, A.E. Ehlers, E.J. Baerends, *J. Chem. Phys.* 110 (1999) 8943.
- [18] (a) P. Hohenberg, W. Kohn, *Phys. Rev. B* 136 (1964) 864;
(b) W. Kohn, L.J. Sham, *Phys. Rev. A* 140 (1965) 1133;
(c) J.C. Slater, *Quantum Theory of Molecules and Solids*, vol. 4, McGraw-Hill, New York, 1974;
(d) S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [19] (a) N. Godbout, D.R. Salahub, J. Andzelm, E. Wimmer, *Can. J. Chem.* 70 (1992) 560;
(b) C. Sosa, J. Andzelm, B.C. Elkin, E. Wimmer, K.D. Dobbs, D.A. Dixon, *J. Phys. Chem.* 96 (1992) 6630.
- [20] L.A. Curtiss, P.C. Redfern, D.J. Frurip, *J. Comput. Chem.* 15 (2000) 147.
- [21] L.A. Curtiss, P.C. Redfern, K. Raghavachari, V. Rassolov, J.A. Pople, *J. Chem. Phys.* 110 (1999) 4703.
- [22] L.A. Curtiss, P.C. Redfern, V. Rassolov, G. Kedziora, J.A. Pople, *J. Chem. Phys.* 114 (2001) 9287.
- [23] (a) V. Barone, M. Cossi, *J. Phys. Chem. A* 102 (1998) 1995;
(b) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* 24 (2003) 669.
- [24] (a) A. Klamt, A.G. Schuurmann, *J. Chem. Soc., Perkin Trans.* (1993) 799;
(b) A. Klamt, *J. Phys. Chem.* 99 (1995) 2224;
(c) A. Klamt, V. Jones, *J. Chem. Phys.* 105 (1996) 9972;
(d) C.C. Pye, T. Ziegler, *Theor. Chem. Acc.* 101 (1999) 396.
- [25] Y. Takano, K.N. Houk, *J. Chem. Theory Comput.* 1 (2005) 70.
- [26] A. Klamt, V. Jonas, T. Burger, J.C.W. Lohrenz, *J. Phys. Chem. A* 102 (1998) 5074.
- [27] A. Bondi, *J. Phys. Chem.* 68 (1964) 441.
- [28] C.J. Cramer, *Essentials of Computational Chemistry: Theories and Models*, second ed., Wiley Chichester, England, 2004.
- [29] W.E. Acree Jr., S.A. Tucker, M.D. Ribeiro da Silva, M.D.M.C. Matos, A.R. Gonçalves, M.A.V. Ribeiro da Silva, *J. Chem. Thermodyn.* 27 (1995) 391.
- [30] A. Haaland, H. Thomassen, Y. Stenström, *J. Mol. Struct.* 263 (1991) 299.
- [31] (a) O. Kniemeyer, J. Heider, *J. Biol. Chem.* 276 (2001) 21381;
(b) H.A. Johnson, D.A. Pelletier, A.M. Spormann, *J. Bacteriol.* 183 (2001) 4536.
- [32] (a) C.W. Bauschlicher, *Chem. Phys. Lett.* 246 (1995) 40;
(b) L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, *J. Chem. Phys.* 106 (1997) 1063;
(c) L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, *J. Chem. Phys.* 112 (2000) 7374;
(d) L.A. Curtiss, P.C. Redfern, K. Raghavachari, *J. Chem. Phys.* 123 (2005) 124107.
- [33] G.N. George, K.J. Nelson, H.H. Harris, C.J. Doonan, K.V. Rajagopalan, *Inorg. Chem.* 46 (2007) 3097.
- [34] Y. Takano, K.N. Houk, *J. Chem. Theory Comput.* 1 (2005) 70.
- [35] This stepwise approach has been used elsewhere as, for example, in the calculation of pK_a values: (a) M.D. Liptak, G.C. Shields, *J. Am. Chem. Soc.* 123 (2001) 7314;
(b) M.D. Liptak, G.C. Shields, *Int. J. Quant. Chem.* 85 (2001) 727;
(c) M.D. Liptak, K.C. Gross, P.G. Seybold, S. Feldgus, G.C. Shields, *J. Am. Chem. Soc.* 124 (2002) 6421.
- [36] R.E. Brown, F. Barber, *J. Phys. Chem.* 99 (1995) 8071, In the work, bisulfite is favored over sulfonate by ca. 4 kcal/mol.
- [37] (a) X.-B. Wang, J.B. Nicholas, L.-S. Wang, *J. Chem. Phys.* 113 (2000) 10837;
(b) M.L. McKee, *J. Phys. Chem.* 100 (1996) 3473;
(c) A.T. Blades, P. Kebarle, *J. Am. Chem. Soc.* 116 (1994) 10761.
- [38] R.H. Holm, *Coord. Chem. Rev.* 100 (1990) 183.
- [39] J.H. Espenson, *Adv. Inorg. Chem.* 54 (2003) 157.
- [40] W. Nam, *Accounts Chem. Res.* 40 (2007) 522.
- [41] G.D. Watt, J.W. McDonald, W.E. Newton, *J. Less-Common Met.* 54 (1977) 415.
- [42] (a) B.E. Schultz, S.F. Gheller, M.C. Muetterties, M.J. Scott, R.H. Holm, *J. Am. Chem. Soc.* 115 (1993) 2714;
(b) B.E. Schultz, R.H. Holm, *Inorg. Chem.* 32 (1993) 4244.
- [43] M.K. Johnson, D.C. Rees, M.W.W. Adams, *Chem. Rev.* 96 (1996) 2817.
- [44] R. Hille, *Trends Biochem. Sci.* 27 (2002) 360.
- [45] L. Huang, B. Zhuang, Y. Yang, J. Lu, *Jiegou Huaxue (Chinese J. Struct. Chem.)* 5 (1986) 124.
- [46] J.M. Berg, K.O. Hodgson, *Inorg. Chem.* 19 (1980) 2180.

- [47] K. Unoura, M. Kondo, A. Nagasawa, M. Kanesato, H. Sakiyama, A. Oyama, H. Horiuchi, E. Nishida, T. Kondo, *Inorg. Chim. Acta* 357 (2004) 1265.
- [48] (a) S.C. Lee, unpublished results;
(b) J.-J. Wang, S. Groysman, S.C. Lee, R.H. Holm, *J. Am. Chem. Soc.* 129 (2007) 7512.
- [49] L.M. Thomson, M.B. Hall, *J. Am. Chem. Soc.* 123 (2001) 3995.
- [50] O. González-Blanco, V. Branchadell, K. Monteyne, T. Ziegler, *Inorg. Chem.* 37 (1998) 1744.