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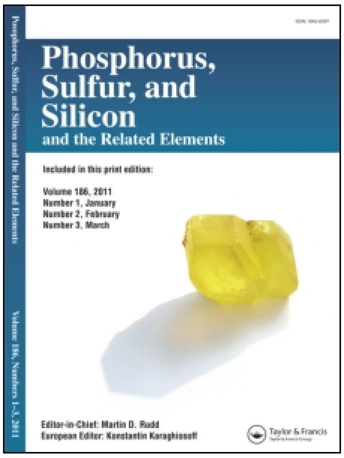

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Publication details, including instructions for authors and subscription information:
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Calculation of the Standard Potentials of the Dithiocarbamate/thiuram Disulfide Redox System via Thermochemical Cycles and Computational Electrochemistry

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Online publication date: 27 October 2010

To cite this Article Lieder, Marek(2003) 'Calculation of the Standard Potentials of the Dithiocarbamate/thiuram Disulfide Redox System via Thermochemical Cycles and Computational Electrochemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 1, 179 — 189

To link to this Article: DOI: 10.1080/10426500307784

URL: http://dx.doi.org/10.1080/10426500307784

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Phosphorus, Sulfur and Silicon, 2003, Vol. 178:179–189
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1042-6507/03 $12.00 + .00
DOI: 10.1080/10426500390170327

CALCULATION OF THE STANDARD POTENTIALS OF THE DITHIOCARBAMATE/THIURAM DISULFIDE REDOX SYSTEM VIA THERMOCHEMICAL CYCLES AND COMPUTATIONAL ELECTROCHEMISTRY

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(Received May 10, 2002; accepted June 9, 2002)

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Ab initio and density functional levels of electronic structure theory are applied to calculate the standard potentials of alternative routes for the oxidation of dithiocarbamic anions and the reductive cleavage of thiuram disulfide. The reactions are modeled with dithiocarbamic acid H_2NCS_2H and thiuram disulfide $(H_2NCS_2)_2$. Aqueous and DMSO solvation effects are included using IPCM and PCM continuum solvation models. A pathway proceeding via a single electron detachment followed by radical dimerization is predicted to be the most favorable mechanism for dithiocarbamic anion (or acid) oxidation. Two pathways of the reduction of thiuram disulfides are tested. In the gas phase the reaction is more likely (energetically preferred) to proceed in a stepwise manner, that is, the electron attachment is followed by the S—S bond splitting. In the solvent environments the concerted bond breaking electron transfer mechanism is predicted to potentially be equally probable.

Keywords: Computational modeling; dithiocarbamates; electrochemistry; standard potentials; thermochemical cycles; thiuram disulfides

INTRODUCTION

The electrochemical properties of dithiocarbamic complexes, particularly of highly oxidized metal cations, have been under thorough scrutiny owing to their various potential applications and many challenging traits.[1] The ligands themselves, however, currently are less often studied since their electrochemical oxidation at mercury and solid electrodes seems to be roughly established.[2–7] At inert surfaces, such as

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This work was supported by The Technical University Gdansk. The author is very grateful for the possibility of using facilities of the CI TASK Computing Center in Gdańsk.

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platinum, gold, and vitreous carbon, oxidation of dithiocarbamates proceeds in a few electrochemical and chemical steps leading to a final thiuram disulfide product. It recently has been shown that the adsorption of intermediates at gold and glassy carbon electrodes also contributes to the reaction kinetics.[8] While there is no doubt that thiuram disulfide is the final product of the oxidation, pathways other than a single electron transfer followed by free radicals coupling are usually not considered due to great difficulty in distinguishing between alternative mechanisms. At a mercury electrode, the formation of mercury complexes is usually involved. That is, oxidation of the mercury electrode occurs in preference to oxidation of the ligand. The ultimate products from the oxidation step depend on the relative stability of the complexes in the different oxidation states of mercury.[9]

The most comprehensive studies to date of thiuram disulfide reduction were carried out by Visco and coworkers.[10] They analyzed possible routes of the process from the electrochemical experiments data (cyclic voltammetry, chronoamperometry) but gave no direct answer which route is preferred by system.

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Since a complex model for the redox properties of the dithiocarbamate/thiuram disulfide system still waits to be presented the author's aim was to address this problem by considering the standard potentials of the possible reactions and their energetics. Redox potentials are usually derived from cyclic voltammetry experiments provided the electron-transfer process is reversible. For non-reversible reactions the experimental situation is more complicated, and accurate values are only available through very rapid techniques like, for example, pulse radiolysis.[11] The redox potentials, however, can be derived using the Hess's law from other thermochemical data like the energy differences in reagents formation, heterolysis and homolysis of bonds, and solvation of ions or molecules.[12–14] These data were computed or, if available, taken form reported experiments.[15] The standard potentials are typically reported relative to a reference electrode, usually taken as the standard hydrogen electrode. The free energy change associated with the SHE half-reaction is −4.44 eV.[16]

Because of the computational expense, dithiocarbamic acid H_2NCS_2H (**RSH**) and thiuram disulfide $(H_2NCS_2)_2$ (**RS-SR**) were chosen as model compounds.

COMPUTATIONAL METHODS

All molecular geometries were optimized in the gas phase at the Hartree-Fock (HF) level of theory, using the 6-31(d) basis set. Unrestricted HF theory was used for all open-shell systems. For the radicals considered here, spin contamination was very small, if present at all, and calculated $\langle S^2 \rangle$ values were less than 0.78. Analytical evaluation of the Hessian matrix for the HF geometries was used in order to determine the zero-point vibrational energy to characterize the type of stationary point, and thermal contributions to the enthalpy and free energy at 298K.

Single-point calculations of the absolute free energies employed the gas phase HF/6-31(d) geometries and were carried out using the gradient-corrected density functionals of Becke[17] for exchange and of Perdew and Wang[18] for correlation. This combination of density functionals is referred to as BPW91. Computations use the Double-Zeta-Valence Polarized basis set (aug-cc-pVDZ),[19,20] which is specially designed for DFT calculations.[21] Standard state solvation free energies in water (dielectric constant $\varepsilon = 78.3$) and in DMSO ($\varepsilon = 46.7$) were calculated using the polarized continuum model (PCM) and the isodensity polarized continuum model (IPCM).[22,23] The former model defines the cavity as the union of a series of interlocking atomic spheres, whereas the latter model defines the cavity as an isodensity surface of the molecule. An isodensity surface is a very natural, intuitive shape for the cavity since it corresponds to the reactive shape of the molecule to as great a degree as possible (rather than being a simpler, predefined shape such as a sphere or a set of overlapping spheres). For comparison the calculations of solvation free energies in aqueous solutions were carried out using the Langevin Dipoles (LD) solvation model.[24] In this model the solvent is approximated by polarizable dipoles fixed on a cubic grid. The calculations were carried out with the Gaussian 98 ver. A9 molecular orbital packages,[25] and Chemsol 2.1.[26]

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RESULTS AND DISCUSSION

Standard Potential Computation

Table I lists computed and calculated data (where experimental data are available) the standard free energies and the standard potentials of the reactions proceeding in gas phase and in aqueous or DMSO solutions. The computed values can be derived from the data provided in Tables II and III. Because experimental data of solvation energies for the involved species are not available its hard to evaluate the accuracy of the used models. The LD model is reported to be very well suited for the sulfur compounds.[27] In our case the LD model calculations give higher solvation energies relative to the two other models, particularly for the charged species. The presented standard potentials do not carry any information about the possible interaction with the electrode

TABLE I Theoretical and Experimental Thermochemistry of Redox Processes of Dithiocarbamates and Thiuram Disulfides

Process	Phase	Thermochemical quantity	Expt[b]	Solvation theory[a]		
				IPCM	PCM	LD
1 $RSH \rightarrow RS^{\cdot} + H^{+} + e$	Gas	$\Delta G^{0}_{(g)}$	16.44[c]			
	Aqueous	$E^{\phi}_{1,aq}$	0.79	0.86	0.84	0.40
	DMSO	$E^{\phi}_{1,dmso}$	0.56	0.65	0.64	
2 $RS^{\cdot} \rightarrow RS^{\cdot} + e$	Gas	$-\Delta G^{0}(EA)$	2.30[c]			
	Aqueous	$E^{\phi}_{2,aq}$	0.58	0.21	0.28	0.49
	DMSO	$E^{\phi}_{2,dmso}$	0.30	0.21	0.25	
3 $2RS^{-} \rightarrow RS\text{-}SR^{\cdot -} + e$	Gas	$\Delta G^{0}_{(g)}$	1.81[c]			
	Aqueous	$E^{\phi}_{3,aq}$		0.37	0.77	1.07
	DMSO	$E^{\phi}_{3,aq}$		0.37	0.77	
4 $RS^{\cdot} \rightarrow RS^{+} + e$	Gas	$\Delta G^{0}(IE)$	8.04[c]			
	Aqueous	$E^{\phi}_{4,aq}$		1.05	1.28	1.27
	DMSO	$E^{\phi}_{4,dmso}$		1.05	1.31	
4 $RS\text{-}SR \rightarrow RS\text{-}SR^{\cdot +} + e$	Gas	$\Delta G^{0}(IE)$	8.17[c]			
	Aqueous	$E^{\phi}_{5,aq}$		2.08	1.89	1.71
	DMSO	$E^{\phi}_{5,dmso}$		2.07	1.93	
6 $RS\text{-}SR + e \rightarrow RSSR^{\cdot\cdot}$	Gas	$\Delta G^{0}(IE)$	−2.04[c]			
	Aqueous	$E^{\phi}_{6,aq}$		−0.75	−0.66	−0.38
	DMSO	$E^{\phi}_{6,dmso}$		−0.74	−0.70	
7 $RS\text{-}SR + e \rightarrow RS^{\cdot} + RS^{\cdot}$	Gas	$\Delta G^{0}_{(g)}$	−1.55[c]			
	Aqueous	$E^{\phi}_{7,aq}$	−0.59	−0.59	−0.17	0.20
	DMSO	$E^{\phi}_{7,aq}$	−0.87	−0.58	−0.18	

[a] Computed from data in Tables II and III.

[b] Potentials calculated from thermochemical experimental data.

[c] Computed from data in Table III; standard potentials vs. SHE in V, all other thermochemical quantities in eV.

surface, which is likely and might drive the potential to more negative values (depending, of course, on the substrate metal), although they quite well correlate with experimental oxidation or reduction peak potentials obtained by the cyclic voltammetry.[28,29] The relatively low redox potential of reaction **2** reflects high stability of the free radical owing to the resonance stabilization of an unpaired electron between two sulfur atoms.

The experimental standard potential of the redox reactions **1–7** are not known. The potentials of the reactions **1**, **2**, and **7** can be estimated from available thermochemical data according to a well known procedure,[12,13] which is a combination of the Gibbs energy of RS—H

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TABLE II Theoretical Free Energy of Solvation

	Method				
	IPCM		PCM		LD
Molecule	Aqueous	DMSO	Aqueous	DMSO	Aqueous
RSH	−8.8[1]	−8.6	−9.1	−9.7	−3.3
RS^-	−60.4	−59.8	−62.5	−62.6	−72.0
$RS^\cdot$	−5.8	−5.7	−6.4	−7.1	−10.8
RS^+	−65.2	−64.6	−61.2	−61.3	−65.5
RSSR	−12.6	−12.4	−6.1	−7.3	−11.1
$RSSR^-$	−50.2	−49.7	−45.9	−46.7	−58.4
$RSSR^+$	−50.7	−50.2	−48.8	−49	−57.4

[1] kcal mol^{-1}.

bond homolysis, pK_a(RSH),[30*] and the standard potential of the H^+/H^+ couple.[15,31] The S—H bond dissociation energy necessary for this calculation is uncertain because it has not been measured directly. In the sturated thiols the S—H bond enthalpy is 92 kcal mol^{-1}, independent of the nature of the alkyl chain.[32] Phenyl exerts a bond weakening effect on adjacent S—H bond of ca. 10 kcal mol^{-1} reflecting a delocalization of the ring electrons and charge donation to the radical center. A stronger weakening impact of ca. 22 kcal mol^{-1} exerts adjacent sulfur in the higher sulfanes H_2S_{n+1}. The latter value is very close to the computed resonance energy in $CH_3C(=S)S—H$ (ca. 18 kcal mol^{-1}).[33] Therefore, the "experimental" values of the standard potentials were estimated using $\Delta H_D(S—H) = 72$ kcal mol^{-1}.

Reaction **1** $E_1^{\phi} = \Delta G_D(S—H)^{\#} + E^{\phi}_{H^+/H^+}$

Reaction **2** $E_2^{\phi} = \Delta G_D(S—H) - 2.3RTpK_a + E^{\phi}_{H^+/H^+}$

Reaction **7** $E_7^{\phi} = E_2^{\phi} - \Delta G_D(S—S)$

The S—S bond dissociation free energy used for calculation is 27 ± 3 kcal mol^{-1}.[34]

[*] The pK_a(DMSO) value of RSH was estimated from $pK_a(H_2O)$ of $(C_2H_5)_2NC(S)SH$. The reported acidities of benzenethiols and aliphatic thiols are higher in H_2O than in DMSO.[43] This change is primarily attributed to the strong H-bond donor properties of the water solvent, which achieve maximum effectiveness toward localized anions. Accordingly, the acidity difference is large for n-butanethiol ($pK_a = 17.03$ and 10.88) and relatively low for 4-nitrobenzenethiol ($pK_a = 5.5$ and 4.7), which forms a highly delocalized anion. Assuming that the observed differences in acidities reflects mainly charge delocalization in the anions, and to lesser extent a molecular neighborhood of the —SH group, we have plotted a correlation line between thiol acidities in both solvents,[43,44] from which the $pK_a(DMSO) = 4.5$ of the studied compound was read out.

[#] eV.

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TABLE III Calculated Electronic Energies, Thermal Energy Corrections to Gibbs Free Energy, and Absolute Entropies

Molecule	Total energy BPW91[a,b]			TEC[a,c]	S^{c}(gas)[d]
	Gas	Aqueous	DMSO		
RSH	−891.088497	−891.102451	−891.102176	0.015067	66.5
RSH$^{\cdot-}$	−891.093718	−891.185889	−891.184989	0.009777	67.6
RS$^{\cdot}$	−890.562038	−890.658315	−890.657348	0.007155	66.8
RS$^{\cdot}$	−890.475050	−890.484361	−890.484174	0.004568	67.6
RS$^{\cdot}$ (vert)	−890.467342	−890.474063	−890.473908	0.007155	—
RS$_{\cdot}^{+}$	−890.183233	−890.287114	−890.286126	0.008270	66.0
RS-SR	−1781.004334	−1781.024457	−1781.024029	0.036134	74.0
RS-SR$^{\cdot-}$	−1781.079609	−1781.159647	−1781.158795	0.036534	76.0
RS-SR$^{\cdot-}$ (vert)	−1781.016269	−1781.097790	−1781.096938	0.036134	—
RS-SR^{2} (vert)	−1781.003732	−1781.272965	−1781.270460	0.036534	—
RS-SR$^{\cdot+}$	−1780.705138	−1780.785919	−1780.785128	0.037169	75.3

[a] Units of hartree.

[b] BPW91/aug-cc-pVDZ.

[c] Thermal energy correction to Gibbs free energy.

[d] cal mol^{-1} K^{-1}.

Thermodynamics of the Reactions

The reactions **1–7** comprise major charge transfer process in the considered system. They do not contain dimerization or other coupling reactions between radicals or ions. These coupling reactions may also involve chemisorption at the electrode surface, which is not considered (thiol radicals adsorb at the metal surfaces[35]), or reactions with the surrounding solvent. The latter process might involve H-atom transfer to the RS^{-} radical. It seems, however, that in aqueous or DMSO solutions such a transfer is unlikely due much higher O—H (ca. 119.2 kcal mol^{-1}[36]) and C—H (98 kcal mol^{-1}) bond dissociation enthalpy in water and DMSO, respectively, in comparison to S—H bond in dithiocarbamic acid (ca. 72 kcal mol^{-1}, this work).

The various possible steps in the dithiocarbamate oxidation and the products reductive cleavage are detailed in Figure 1, with free energies differences in gas and aqueous environment. Apart from equilibrated species, there are also shown in the figure various excited intermediated species ions produced by vertical electron attachment.

We begin by considering the oxidation of RS$'$ by a single electron detachment. In the gas phase the reaction is endergonic because anionic form has higher resonance stabilization energy relative to the radical molecule. The net endergonicity after relaxation is 53.0 kcal mol^{-1}. The aqueous solution strongly stabilizes the anions as expected, therefore

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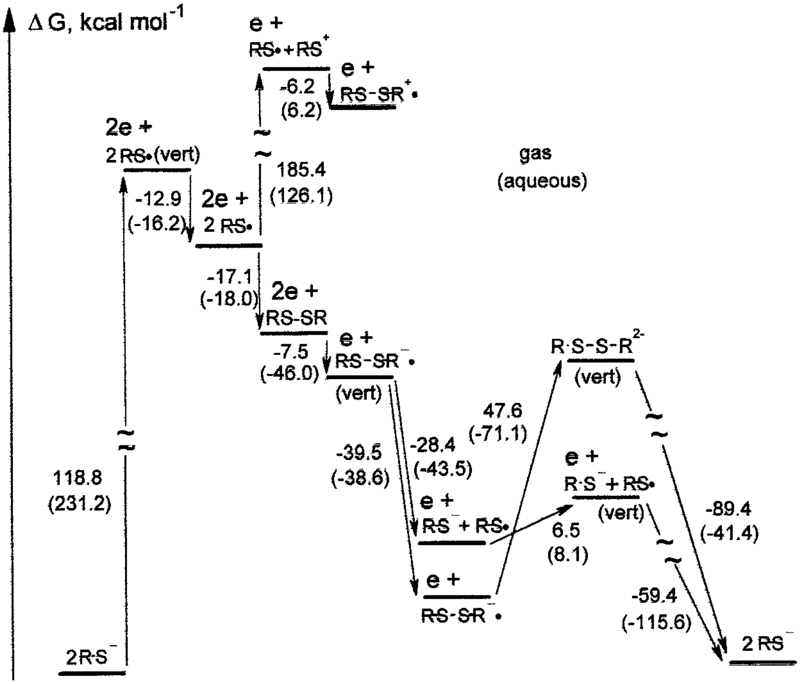

FIGURE 1 Relative free energies in eV in the gas phase (in aqueous solution) for intermediates in the oxidation for dithiocarbamic anions and reductive cleavage of the S–S bond in thiuram disulfide. Compounds labeled (vert) denote nascent species produced by vertical electron attachment. The energy levels are scaled to the gas phase energetics.

the reaction endergonicity is 107.5 kcal mol^{-1}. The structure of the RS′ radical differs from the parent anion with shorter C—N bond by ca. 0.3Å and with smaller S—C—S angle, which decreases from 127.8 to 109.1°. The next step would be a chemical reaction of radicals dimerization resulting in RS-SR formation or anion-radical recombination to $RS\text{-}SR^-$. The former route is exergonic by ca. −18 kcal mol^{-1} and remains practically unaffected by the change of the surrounding environment. The latter path, however, seems a realistic alternative in the gas-phase (−11.1 kcal mol^{-1}, see "a deep valley" in Figure 1). In the aqueous solution this route seems unlikely due to its endergonicity by 4.9 kcal mol^{-1}. These results are consistent with the cyclic voltammetry experiments, which show a single irreversible oxidative peak while driving the electrode potential up to 1 V vs. SHE [7,28,37]. At higher potentials there are two theoretically possible reactions; the radical oxidation to dithiocarbamic cation followed by the coupling to RS-SR,

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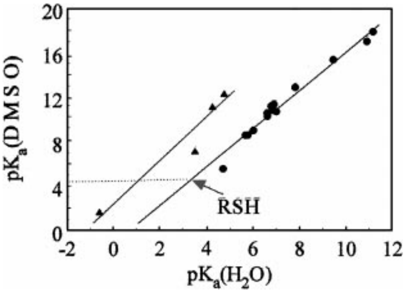

FIGURE 2 pK_a values for benzenethiols, liphatic thiols, and oxygen acids. The extrapolated pK_a (DMSO) for RSH is 4.5.

alternatively to RS-SR$^{\cdot+}$ or, at much more positive potentials (ca. 2 V), the oxidation of RS-SR to RS-SR$^{\cdot+}$. Further oxidation of dithiocarbamates (thiuram disulfides) to cyclic five member dications has been reported to achieve by the chemical oxidation with iodine (structure confirmed by x-ray analysis)[38] and apparently by the electrochemical oxidation at platinum.[4] Our results indicate that this process is more likely to proceed via the RS-SR oxidation (free radicals are probably more eager to the chemical coupling), although this route is not energetically favorable, and is likely to proceed at the verge of the thermodynamic stability of the electrodes and majority of the organic solvents (reaction **4**).

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Another theoretically possible path of the oxidation of dithiocarbamic ions (going from the right hand side of Figure 1) would be anions coupling to RS-SR^{2-} followed by two single electron transfer steps resulting in RS-SR formation. This route, however, is highly endergonic and should result in two oxidative peaks in cyclic voltammograms, which has not been reported.

We turn now to the reductive cleavage of the S—S bond, reactions **6** and **7** in Table I. Thiuram disulfides can be reduced electrochemically, for example in cyclic voltammetry experiments, giving rise to an irreversible one-electron wave due to reaction **6** or **7**.

Upon addition of one electron the cleavage reaction may proceed either as a follow-up chemical heterolysis (reaction **6**) or as a concerted electron transfer-bond breaking process (reaction **7**).

The S—S bond scission in “normal” disulfides is strongly affected by the electrode material and by the molecular surroundings of the S—S bond. For instance, the peak potential of the reduction wave, E_p^{red} of di-*tert*-butyl disulphide is −2.47 V, whereas E_p^{red} of diphenyl disulphide is only −1.36 V vs. SHE due to stabilization effect of the electron delocalization in the free radical and the anion.[39] A similar resonance influence one can expect in the case of dithiocarbamates. Vertical electron attachment is somewhat exergonic (-7.5 kcal mol^{-1}) in gas phase owing to charge delocalization. In water the reaction is much more favorable because of additional stabilization effect of the solvation. The S—S bond dissociation energy (enthalpy) in relaxed RS-SR′ declines relative to RS-SR from 34.0 to 26.7 kcal mol^{-1} in gas and from 35.0 to only ~10.6 kcal mol^{-1} in liquid phase. The positive values, however, indicate that the free radical anion is thermodynamically stable. The S—S separation increases to 2.941 Å, whereas in RS-SR it is only 2.064 Å. In both calculations, the C—S—S—C dihedral angle remains near 90° and changes in the S—C and C—N distances from the parent compound are minimal. These observations are consistent with MeS—SMe″ and other alkyl disulfides radical anions studies which explain the S—S bond distance increase to the location of the unpaired electron in a σ^* orbital formed by the $3p_x$ orbitals of the two S atoms.[40] The net exergonicity relative to the parent form is -47.0 and -84.6 kcal mol^{-1} in gas and aqueous phase respectively. On the other hand the concerted electron transfer is exergonic with the energy gain -35.9 and -89.5 kcal mol^{-1} in the same order of relevance.

Kinetic Aspects of the S—S Bond Cleavage

The kinetic insight into the nature of the reductive cleavage of the S—S bond can be gained by estimating the activation barrier for the both considered pathways. In the case of the stepwise mechanism the outer-sphere electron transfer theory by Marcus and his quadratic relationship was used.[41] The activation energy for the concerted mechanism, however, was calculated with the Savéant equation,[42] which extends the application of the quadratic relationship to the processes resulting in bond breaking. Savéant proposed to use the bond enthalpy of dissociation in place of the inner reorganization energy. Results of these calculations are presented in Table IV.

These results indicate that the activation barrier for the stepwise mechanism is lower than that for the concerted path. Conclusions based on the differences of a few kcalories, however, might be misleading because the Marcus equation does not yield the actual activation barrier. It neglects the resonance energy resulting from the combination of the precursor valence structure and the successor valence structure at the critical configuration, that is, the delocalization energy of the electron between the donor and the acceptor. The Marcus equation is based on the assumption that this energy is small. For reactions other than weak coupling electron-transfer, it is generally not small, particularly if λ is not much greater than ΔG°. As a consequence of these results, we conclude that the reductive cleavage of the S—S bond in the aqueous

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TABLE IV Calculated Thermodynamic and Kinetic Parameters of the Reductive Cleavage of the S—S Bond (kcal mol^{-1})

	λ_0^1	λ_1	BDE	ΔG^0_{step}	ΔG^0_{conc}	ΔG^{++}_s	ΔG^{++}_c
Vacuum	—	39.7	34.0	−47.0	−35.9	*	*
H_2O	14.8	38.8	35.0	−84.6	−89.5	4.5	7.9
DMSO	12.8	38.8	34.9	−84.3	−89.0	5.2	8.9

*The Marcus theory is not applicable to gas phase reactions. λ_0—solvent reorganization energy, calculated from N × Pk × (1/2a-1/2R), where Pk is a Peckar factor, a—the cavity radii for the thiuram disulfide (4.5 Angst); R—separation of the redox species and its image in the metal electrode $\{2(a + d_{solv})\}$; d_{solv}—solvent molecule diameter; N—normalization factor. λ_i—inner reorganization energy, calculated from E(radical anion at optimized neutral geometry, vertical)—E(optimized radical anion). BDE—the S—S bond dissociation energy (enthalpy). ΔG^0—the free energy (the driving force) of the redox reaction for the stepwise (s) and concerted (c) mechanism.

or DMSO environment is more likely to proceed via stepwise manner, but the concerted mechanism can not be excluded solely by the kinetic findings.

Conclusions

Standard potentials and energetics related to the reactions of the dithiocarbamic acid (or anion) oxidation and the thiuram disulfide reduction can be evaluated by electronic structure calculations at the BPW91/DZVP level comprising the solvation effects from water or DMSO (PCM, IPCM continuum models). In the solvent media the oxidation proceeds mainly via free electron formation followed by the dimerization resulting in thiuram disulfide.

Two mechanisms of the reductive cleavage of the S—S bond in thiuram disulfides are considered. In the gas phase the reaction is more likely to proceed in a stepwise manner, that is, the electron attachment is followed by the S—S bond splitting. This mechanism is favored energetically and it is supported by the stability (relatively large dissociation enthalpy of the S—S bond) of the intermediate free radical anion.

In the solvent environments the concerted bond breaking electron transfer mechanism is predicted to potentially be more probably (thermodynamically favored). The kinetic analysis, however, does not support this supposition.

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