

Electronic Supplementary Information

Identification of dimethyl sulfide in dimethyl sulfoxide and implications for metal-thiolate disulfide exchange reactions

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I. General considerations

All experiments were carried out in air unless otherwise noted. 1,4 -Dioxane (Sigma Aldrich, anhydrous, 99.8%), n-pentane (Sigma Aldrich, anhydrous, $\geq 99\%$), dimethyl sulfide (DMS) (Sigma Aldrich, anhydrous, $\geq 99\%$), acetonitrile (J.T Baker), absolute ethanol (PHARMCO-AAPER), and n-butanol (Sigma Aldrich) were purchased from the indicated suppliers and used as received. 4-Nitrophenyldisulfide was purchased from Sigma Aldrich and purified according to the procedure described below. Elemental analyses were performed by Columbia Analytical Services, Tucson, AZ.

Seven different bottles of DMSO were purchased from the following suppliers and used as received. The numbers in parentheses are used for sample identification in the GC-MS experiments. DMSO (#1) (Sigma Aldrich; ACS reagent, $\geq 99.9\%$, Lot No. SHBB6833V); DMSO (#2) (Sigma Aldrich; Anhydrous, $\geq 99.9\%$, Lot No. SHBC3339V); DMSO (#3) (Sigma Aldrich; CHROMASOLV[®] Plus, for HPLC, $\geq 99.7\%$, Lot No. SHBB7695V); DMSO (#4) (Acros Organics; extra dry, 99.7% +); DMSO (#5) (Burdick & Jackson; anhydrous solvent, $>99.9\%$); DMSO (#6) [EMD; Ominisolve (High purity solvent $> 99.99\%$)]; and DMSO-*d*₆(#7) [Cambridge Isotope Labs;(D, 99.9%),Chemical purity specification $\geq 99.5\%$].

UV-visible spectra were recorded on a Perkin Elmer Lambda 25 UV/Visible spectrophotometer at 25 °C operating with UV WinLab software. Reactions for UV-Vis studies were carried out in screw cap 1×1 cm cuvettes. GC-MS analyses were performed using a Thermo Scientific Trace GC Ultra gas chromatograph and Thermo Scientific ISQ mass spectrometer. Compound separation was achieved with a PLOT Q column (30 m × 0.32 mm i.d, nonpolar column incorporating 100% divinylbenzene × 10 μm df capacity film thickness, Restek Corp., Bellefonte, PA, USA). The column flow rate was 2 mL/min. The oven temperature was held at 80 °C for 1 min, then increased to 160 °C at a rate of 40 °C/min and held for eight min, followed by an increase to 270 °C at a rate of 40 °C/min, and held for 7 min. The injector, MS transfer line, and ion source temperatures were 200, 250, and 200 °C, respectively. Electron ionization mass spectrometric data from m/z 50 to 300 amu were collected using an ionization voltage of 70 eV. Compound identifications were made by comparing mass spectral patterns with those from known samples and the use of the NIST 2008 mass spectral database.

II. GC-MS experiments

Because DMS-free DMSO was not available, calibration standards were prepared from varying proportions of a 2.7 mM DMS in dioxane solution, 1.00 mL of an 8.6 mM pentane in dioxane solution (included as an internal standard), and diluted to 10.00 mL with dioxane, to span the 0.07 to 1.0 mM DMS concentration range. Unknowns were prepared from the unknown DMSO sample by adding 1.00 mL of the 8.6 mM pentane in dioxane internal standard solution and diluting with dioxane to 10.00 mL. Calibration standards, unknowns, and blanks were injected in triplicate in a standard bracket analysis. The relative response factor of the $m/z = 62$ ion of DMS to the $m/z = 72$ ion of pentane, from extracted ion chromatograms of the standards before and after injection of the unknowns, was used in a weighted least squares analysis to calculate the calibration curve. Interactions between DMSO, DMS and dioxane resulted in a small shift in retention times in the unknowns compared to the standards than contained only DMS and dioxane. A standard addition analysis of DMS (without dioxane) was also performed for one of the samples and gave the same DMS concentration, within experimental uncertainty.

Table S1. Concentration of DMS in commercial samples of DMSO determined by GC-MS

DMSO - commercial samples	DMS (mM +/- 1SD)
Sigma Aldrich, ACS reagent, $\geq 99.9\%$	0.49 (0.11)
Sigma Aldrich, anhydrous, $\geq 99.9\%$	0.47 (0.06)
Sigma Aldrich, CHROMOSOLV [®] Plus, for HPLC, $\geq 99.7\%$	0.55 (0.12)
Acros Organics, extra dry, 99.7% +	0.46 (0.02)
Burdick & Jackson, anhydrous, $>99.9\%$	0.44 (0.44)
EMD, Omnisolve, $>99.99\%$	0.50 (0.07)
Cambridge Isotope Labs, DMSO-d ₆ (D, 99.9%; chemical purity specification $\geq 99.5\%$)	0.35*

*DMS-d₆

III. Purification of bis(4-nitrophenyl)disulfide

A solution of bis(4-nitrophenyl)disulfide (1.00 g, 3.24 mmol) in n-butanol (50 mL) was carefully heated to its boiling point for 30 min in an open system on a hot plate. The system was stoppered with a rubber septum and cooled to room temperature until crystals formed. The supernatant liquid was filtered and disulfide crystals were separated. The pale yellow crystals were washed three times with 30 mL portions of hot ethanol and dried on a boiling water bath under a flow of dry nitrogen. Yield: 0.90 g, 90 %. Elemental analysis: Anal. Calc. for $(\text{SC}_6\text{H}_4\text{NO}_2)_2$ ($M_r = 308.3$): C, 46.74; H, 2.62; N, 9.09; Found: C, 46.74; H, 2.59; N, 9.06. UV-vis in CH_3CN (see Fig. S.1). ^1H NMR (400 MHz, CD_2Cl_2) $\delta = 7.61 - 7.67$ (m, 4H), $8.14 - 8.20$ (m, 4H). FT-IR (see Fig. S.2). Note: it is important to thoroughly dry the crystals to remove all traces of butanol. If any butanol is present, it can protonate the thiolate, which forms as a result of the reaction of DMS with RSSR, rendering the solution colorless or pale yellow. For this reason, only thoroughly dried crystals of disulfide are useful for qualitative testing for the presence of DMS in DMSO.

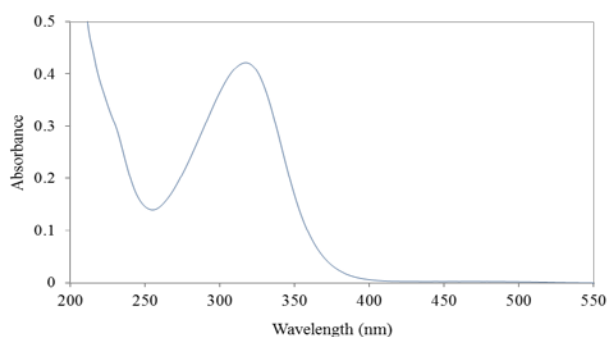


Figure S.1 UV-vis spectrum of purified bis(4-nitrophenyl)disulfide in CH_3CN solution.

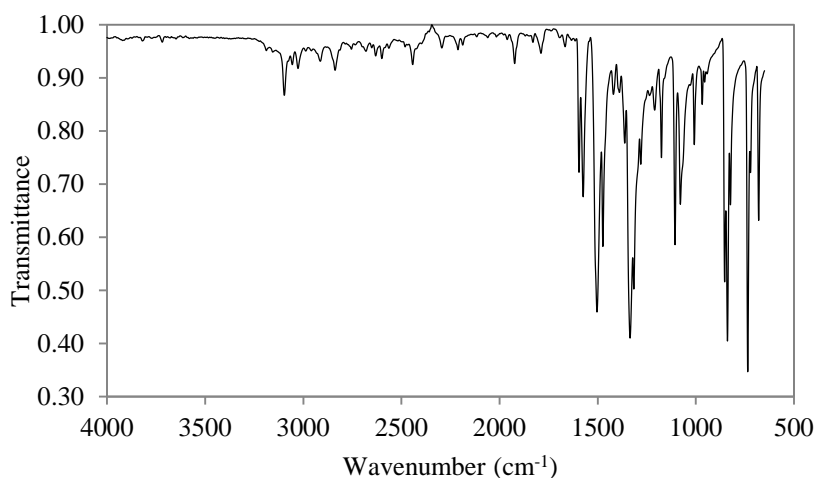


Figure S.2. FT-IR spectrum of purified bis(4-nitrophenyl)disulfide.

IV. Calculations for DMSO disproportionation

Experimental. Reactants and products were built in Gaussview 5.0.8 and optimized in Gaussian09.¹ Optimization and frequency calculations were performed using ground-state DFT with the B3LYP/6-31G+(d) basis set with no symmetry considerations and a restricted wave function. The CPCM model was used both for gas-phase and DMSO solvation. The Gibbs free energy of the reaction was calculated using the shortcut method as described by Otcherski,² and reproduced below.

$$\Delta_r G^\circ = ([\varepsilon_0 + G_{corr}]_{DMS} + [\varepsilon_0 + G_{corr}]_{DMSO2}) - 2 \times [\varepsilon_0 + G_{corr}]_{DMSO}$$

$\varepsilon = 0$, kJ/mol

	$\varepsilon=0$		
	DMS	DMSO	DMSO2
ε_0	-1242854.8	-1438312.4	-1633899.1
εZPE	198.0	207.2	222.0
Etot	210.7	221.9	238.0
Hcorr	213.1	224.4	240.5
Gcorr	127.6	133.4	146.0
$\varepsilon_0 + \varepsilon ZPE$	-1242658.5	-1438149.3	-1633699.1
$\varepsilon_0 + Etot$	-1242645.9	-1438134.6	-1633683.1
$\varepsilon_0 + Hcorr$	-1242643.4	-1438132.1	-1633680.6
$\varepsilon_0 + Gcorr$	-1242728.9	-1438223.1	-1633775.1

$$\Delta_r G^\circ = (-1242728.867 + -1633775.078) - 2 \times (-1438223.111)$$

$$= -57.7226 \text{ kJ/mol}$$

$$\epsilon = 46.83, \text{ kJ/mol}$$

	$\epsilon=46.83$		
	DMS	DMSO	DMSO2
ϵ_0	-1242856.4	-1438312.0	-1633898.6
ϵ_{ZPE}	197.8	207.2	222.0
E_{tot}	210.6	221.9	238.0
H_{corr}	213.0	224.4	240.5
G_{corr}	127.4	133.4	146.0
$\epsilon_0 + \epsilon_{\text{ZPE}}$	-1242658.5	-1438148.9	-1633698.6
$\epsilon_0 + E_{\text{tot}}$	-1242645.8	-1438134.2	-1633682.6
$\epsilon_0 + H_{\text{corr}}$	-1242643.4	-1438131.7	-1633680.2
$\epsilon_0 + G_{\text{corr}}$	-1242728.9	-1438222.7	-1633774.6

$$\begin{aligned} \Delta_r G^\circ &= (-1242728.95 + -1633774.607) - 2 \times (-1438222.705) \\ &= -58.1464 \text{ kJ/mol} \end{aligned}$$

References for Supplementary Information.

1. Gaussian 09, Revision 4.1.2, Gaussian, Inc., Wallingford, CT 2009.
2. Ochterski, Joseph W. "Thermochemistry in Gaussian." Gaussian Inc., Pittsburgh, PA (2000): 1-17, accessed 19 February 2015, <http://gaussian.com/g_whitepap/thermo/thermo.pdf>