

Background: Wikipedia citation on sodium dithionite ...

Sodium dithionite (aka sodium hydrosulfite or sodium hydrosulphite) is a toxic, white crystalline powder with a weak sulfurous odor. It is stable under most conditions, although it will decompose in hot water and in acid solutions. It can be obtained by the following reaction:



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Applications [edit]

Industry [edit]

This compound is a water soluble salt, and can be used as a reducing agent in aqueous solutions. It is used as such in some industrial dyeing processes, where an otherwise water-insoluble dye can be reduced into a water-soluble alkali metal salt. The reduction properties of sodium dithionite also eliminate excess dye, residual oxide, and unintended pigments, thereby improving overall colour quality. It can also be used as a bleach, in, for instance, paper pulp, cotton, wool, and kaolin clay.

This chemical can also be used for water treatment, gas purification, cleaning, and stripping. It can also be used in industrial processes as a sulfonating agent or a sodium ion source. In addition to the textile industry, this compound is used in industries concerned with leather, foods, polymers, photography, and many others. Its wide use are attributable to its low toxicity LD 50 at 5 gms/kg, and hence the wide range of applications.

Biological sciences [edit]

Sodium dithionite is often used in physiology experiments as a means of lowering solution's redox potential. (E⁰ ~ -420 mV at pH 7). Potassium ferrioxamide is usually used as an oxidizing chemical in such experiments (E⁰ ~ 436 mV at pH 7). Additionally, sodium dithionite is often used in soil chemistry experiments to determine the amount of iron that is not incorporated in primary silicate minerals. Hence, iron extracted by sodium dithionite is also referred to as "free iron". The strong affinity of the dithionite ion for bi- and trivalent metal cations (M²⁺, M³⁺) allows it to enhance the solubility of iron, and therefore dithionite is a useful chelating agent.

See also [edit]

- Dithionite

External links [edit]

Sodium dithionite	
General	
Dithionous acid, disodium salt	
D-Ox	
Hydrolin	
Reductone	
Sodium dithionite	
Sodium dithionite hydrate	
Sodium hydrosulfite	
Sodium sulfoxylate	
Sulfoxylate	
Vatrolite	
Virtex L	
Other names	
Molecular formula	Na ₂ O ₄ S ₂
Molar mass	174.09714 g mol ⁻¹
Appearance	White to grayish crystalline powder
CAS number	[7775-14-6]
Properties	
Density and phase	2.19 g cm ⁻³ , solid
Solubility in water	soluble
Other solvents	insoluble in alcohol
Melting point	52°C (325 K)
Boiling point	Decomposes
Hazards	
Toxicity	LD 50: 5 g/kg (oral in rats)
Main hazards	flammable solid
Flash Point	90 C (363 K)

DITHIONITE STRUCTURAL FEATURES

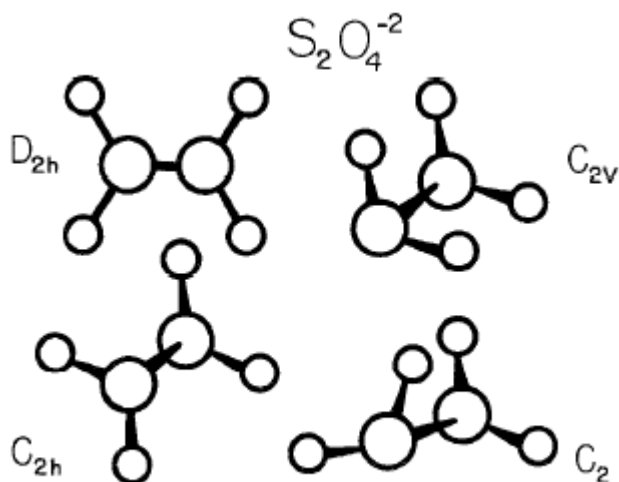


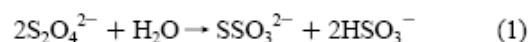
Fig. 1. Four possible structures of the dithionite ion.

Various Isomers of Dithionous Acid

TABLE 1: Average Bond Lengths (pm), Valence Angles (deg), and OSSO Torsion Angles τ (deg) of the $S_2O_4^{2-}$ Anion in Various Dithionites As Determined by X-ray Crystallography (for *cis*- $S_2O_4^{2-}$ $\tau = 0^\circ$; Site Symmetries Are Given; py = pyridine)

cation	S-S	S-O	O-S-O	S-S-O	τ (OSSO)	ref
Na ⁺	239.3	150.2	108.6	99.0	16 (C_2)	7
Na ⁺ (2H ₂ O)	229.8	150.4	109.4	97.5	56 (C_2)	10
Zn ²⁺ (py)	238.6	151.4	110.4	96.7	0 (C_2)	8
Sn ²⁺	235.0	151.0	109.8	96.6	≈ 0 (C_{2v})	9

The two most serious problems with the production of sodium dithionite are its high reactivity toward oxygen (O₂) and its acid-promoted decomposition, which at 20 °C and pH values near 6 proceeds basically according to eq 1 to give thiosulfate and sulfite.¹³



From Meyer et al, *J. Molec. Struct.* 1982

From Steudel et al, *J. Phys.Chem.*, 1998.

DITHIONITE SOLUTION BEHAVIOUR

Peter and Meyer, *J. Molec. Struct.*, 1982: Comparison of the Raman spectra of solid Na₂S₂O₄ with aqueous solution determines that the solid state structure (C_{2v}) changes to (C_{2h}) when dissolved in solution.

Lough and McDonald, *Inorg. Chem.*, 1987: Prepare TetraEthylAmmonium Dithionite [TEAD] for the first time. They report that it is:

*Soluble in non-aqueous solvents (DMF, DMSO and acetonitrile, solutions are air sensitive)

*Yellow solid and is brighter yellow as purity increases (EPR solid $\sim 1\%$ radical SO₂⁻).

*EPR examination of TEAD solutions indicate that a solution equilibrium exists between the dianion dimer and the radical monoanion:

2026 *Inorganic Chemistry*, Vol. 26, No. 13, 1987

Table I. Values of K_{eq} for $[S_2O_4]^{2-} \rightleftharpoons 2[SO_2]^-$ in DMF, Me₂SO, and MeCN at Ambient Temperature

solvent ^a	init $[S_2O_4]^{2-}$ concn, mM	K_{eq} , mM
DMF (36.7)	0.93	30.7
	9.32	204
	21.1	44.0
	26.4	45.3
	93.2	49.8
Me ₂ SO (46.6)	1.30	10.3
	13.0	15.3
	130	8.2
MeCN (36.2)	1.44	20.4
	11.2	10.7
	14.4	8.1
	112	3.8
	144	3.5
H ₂ O ^b (78.5)		1.4×10^{-6}

^aDielectric constant in parentheses. From: Schneider, R. L. *Eastman Org. Chem. Bull.* 1975, 47, 1. ^bFrom ref 3.

$$K_{eq} = [SO_2^-]^2 / ([S_2O_4^{2-}]_{init} - 0.5[SO_2^-]) \quad (2)$$

With initial $[S_2O_4^{2-}] \sim 0.1$ M

Keq ~ 0.050 M in DMF

X = (-0.025 \pm 0.144)/2

And $[SO_2^-] \sim 0.06$ M ?

With $[S_2O_4^{2-}] \sim \rightarrow 0.07$ M ?

How is it possible to have Raman of only $S_2O_4^{2-}$ under these conditions?

Hodgeman, Weinrach and Bennett., Inorg. Chem. 1991: Using samples provided by Lough and McDonald confirm Meyer et al with dianion structural preference for C_{2h} in both aqueous and non aqueous solution (see below).

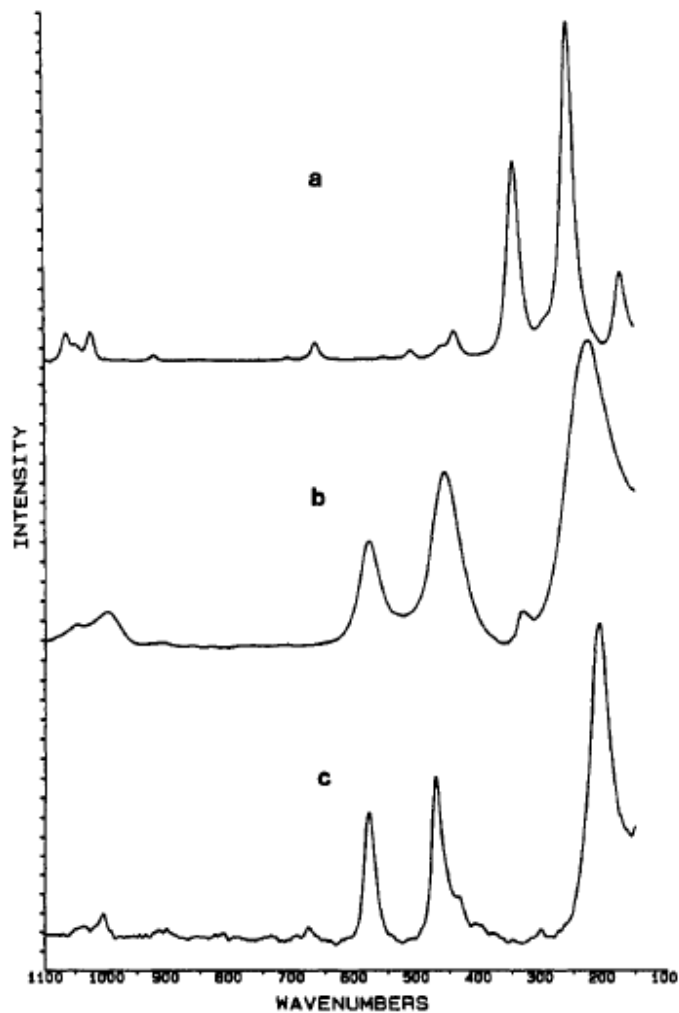


Figure 2. Raman spectra of (a) solid $Na_2S_2O_4$, (b) aqueous $Na_2S_2O_4$, and (c) solid $(Et_4N)_2S_2O_4$.

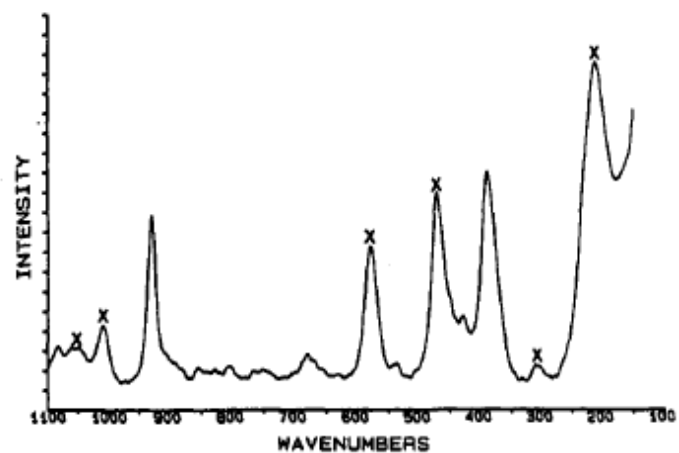


Figure 3. Raman spectrum of $(Et_4N)_2S_2O_4$ dissolved in acetonitrile. Peaks marked with an X are due to $S_2O_4^{2-}$.

Centrosymmetric $S_2O_4^{2-}$ in the Solid State

Table II. Observed and Calculated Frequencies for $S_2O_4^{2-}$ and Potential Energy Contributions of Internal Coordinates

mode	freq, cm^{-1}		contribution to potential energy, %				
	obsd	calcd	S-S str	S-O str	O-S-O bend	S-S-O bend	O_2SSO_2 torsion
B_u	1058	1058		99.7			0.3
B_g	1041	1041		96.6		3.4	
A_g	1005	1005	0.1	93.7	5.5	0.7	
A_u	916	916		93.5	6.4	0.1	
A_g	580	579	4.9	0.6	93.5	1.0	
A_u	575	576		2.6	94.6	2.8	
A_g	472	472	46.5	3.4	4.1	46.0	
B_g	303	303		6.0		94.0	
A_u	...	297		0.2		97.4	0.4
B_u	...	236		0.6		99.0	
A_g	208	209	48.6		0.7	50.7	
B_u	...	171		0.3		0.3	99.4

OTHER REPORTS OF SOLUBLE DITHIONITE SALTS

Mincey and Traylor, BioInorg. Chem., 1978: Sodium dithionite and 18-crown-6 react to give a soluble product ("clear" solution) and evaporate to a white solid that is not distinguished from a simple mixture of the two reactants by IR, 1-H NMR and elemental analysis. Preparation of soluble solutions with other crown ethers and with $[\text{NR}_4]^+$ (R = Me or But) were described as less successful due to problems with purity.

Camps, Coll and Riba, J. C. S. Chem. Commun, 1979: Sodium dithionite solutions for biological testing were prepared by addition of Adogen 464 [methyl, trioctyl ammonium chloride] as a phase transfer reagent and indicate that previous solutions with simpler phase transfer reagents were unsuccessful.

THEORETICAL CALCULATIONS ON THE DITHIONITE ANION

YEAR	GROUP	LEVEL	COMMENT
1982	Passmore / Schriver	CNDO/2	Not even close to reality. Need higher level calculations
<1993	Bennett	STO-3G / 431-G	Positive eigen values (not correct)
1989	Zerner	3-21G* and MP2/3-21G**/3-21G	Rotation of S-S bond requires very small energy change. Staggered conformation the lowest energy rotamer. $\text{C}_{2h} \rightarrow \text{C}_{2v} \Delta E = +38.5 \text{ kJ}$ <i>"We believe that further refinements in the basis set will not change these values greatly."</i>
1993	Bennett	LCAO- $X\alpha$	Rotation of S-S bond requires very small energy change calculated structures related to vibrational spectra.
1998	Steudel	MP2/6-311++G-d,p	Calculations on $\text{H}_2\text{S}_2\text{O}_4$, S-S bond rotation in a shallow saddle point. Other isomers examined.
2002	Passmore / Du	UMPW1PW91/6-31+G*	Not published, full optimization confirms previous work.
2007	Passmore / Mailman	PBE0//6-311G(d) B3LYP	C_{2h} is only true energy minimum $\text{C}_{2h} \rightarrow \text{C}_{2v} \Delta E = +20 \text{ kJ}$ $\text{C1} < \text{C}_{2h} < \text{C2} < \text{C}_{2v}(\text{E}) < \text{D}_{2h} \ll \text{C}_{2v}$
2007	Passmore / Mikko	PBE0//6-311G(d) PBE0//6-311++G(d) aug-CC-pVTZ Aug-CC-pVQZ and B3LYP	PBE0//aug-CC-pVQZ highest level of calculation and gives best match vibrational frequencies. The lower level basis set (6-311G(d)) gave best match to the vibrational intensities.

What we need from the theoretical calculations:

1. Structure / Geometry (fit experimental S-S distance and rotation) where "correct" calculation gives fit with experimental geometry and vibrational frequencies and intensities
2. Good values for the IP / EA of the species involved in the reaction.
3. Energetics of monomer / dimer equilibrium in gas/solid phases for VBT analysis
4. Energetics of monomer / dimer equilibrium in solution $2 [\text{SO}_2]^- \rightleftharpoons [\text{S}_2\text{O}_4]^{2-}$

PASSMORE GROUP SYNTHETIC INTEREST IN DITHIONITE

The Passmore group began using sodium dithionite in 1984 in the reduction of heterocyclic cations in liquid sulphur dioxide. The insolubility of the reducing agent required large excesses of the reagent be used in reduction but allowed for facile removal from the reaction mixture by simple filtration. The reduction by-products were either insoluble $[\text{NaAsF}_6]$ or the solvent SO_2 .

The dithionite reduction reactions were slow and in some cases did not "work" (the recovered products were unreacted starting materials). It appeared that a pattern of reduction was related to the lattice energy.

Cation	m.p. (°C)	Comment on reduction with $\text{Na}_2\text{S}_2\text{O}_4 / \text{SO}_2$
HCSNSCH ⁺	216 (dec.)	No reaction
HCSNSCCH ₃ ⁺	195 (dec.)	No reaction
HCSNSCCF ₃ ⁺	162 (dec.)	Reduction to complex mixture
CF ₃ CSNSCCF ₃ ⁺	230 (dec.)	Quantitative reduction

The H/H and H/CH₃ cations could be reduced in SO_2 solution by the combination of $\text{NMe}_4\text{Cl}/\text{SbPh}_3$ but the products could not be fully separated from the reaction mixture. In general, a soluble reducing agent gives rapid reduction but difficult separation if the products are also soluble. Our initial use of volume based thermodynamics to explain the observed pattern were limited by the level of theoretical calculations (needed for IP / EA and ion volumes) but did show increasing lattice energies for the smaller heterocycles leading to decreasing favorability for the reduction with dithionite.

The synthetic consequence for these calculations was the proposal that a soluble dithionite salt would offer rapid quantitative reduction in SO_2 solution and perhaps a simpler system for separation of the products. The solubility of the dithionite should be directly related to the size of the cation in the salt.

Mailman Preparation of TEAD, internal communication, 2007

A large excess of sodium dithionite (SDT) and tetraethylammonium chloride are loaded into a vessel, sufficient SO_2 is added and the reaction mixture is stirred overnight. The reaction volatiles are removed to precipitate insoluble species generated in reaction. SO_2 recondensed onto the reaction mixture and the soluble materials are removed by filtration and reduced to a clear, yellow oil by evacuation. Dynamic evacuation with mild heating ($T < 100^\circ\text{C}$) produces a beige, soluble solid that can be used as a soluble reducing agent equivalent. **Note:** large excess of dithionite necessary since the reaction is dependent on the surface of the insoluble dithionite salt and as insoluble NaAsF_6 generated further reaction is blocked.

Intended Synthetic Research By Schriver in Passmore Group Summer 2007

The use of volume based thermodynamics to explain the patterns of reactivity of heterocyclic cations in SO_2 provides the weak basis for a publication. The paper would be stronger if ...

- a series of higher level calculations could be used to provide insights into the reduction rxns
- a soluble salt of dithionite could be produced and fully characterized (especially X-ray)
- The soluble dithionite reacted with the suite of cations and new reaction schemes developed

Characterization and Raman Spectrum of "TEAD" Produced in Passmore Group

A sample of TEAD (0.307g) provided by AM/MC was dissolved in SO₂ (0.323g) to give a clear yellow solution. The Raman spectrum was collected at Dal and MAU. No Raman peaks that could be assigned to [S₂O₄]²⁻ were observed in either spectrum. This is not a complete mystery as there are a number of possible compounds that could come from the TEAD preparation that would still be soluble and reducing without being dithionite.

Including: [NR₄] SO₃ salt of decomposition or impurity in dithionite

[NR₄] SO₂ salt of radical anion

[NR₄] SO₂-SO₂ salt of reaction of radical anion with SO₂ (unknown but invoked)

Melting / Decomposition point of TEAD sample > 310 °C (not consistent with lit. and definitely not an ionic liquid.)

A solubility test of the Passmore TEAD sample resulted in a thick yellow oil that on standing at RT for two weeks precipitated clear colourless, thin rectangular crystals (currently in Stan Cameron's hands).

Recrystallisation of Sodium Dithionite

Commercial sodium dithionite is listed as being 85% pure. Meaning it is 15% impure. Several procedures are published for the recrystallization of sodium dithionite. One author noted that the purest dithionite obtained was ~90% and that "recrystallization did not much improve this reaction".

That said, the recrystallization of dithionite according to a literature procedure was done three times and the product used in a preparation of TEAD with no observable improvement in the reaction. This project needs a reputable analysis for dithionite to proceed (in progress).

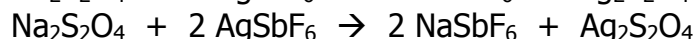
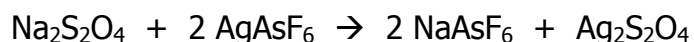
Preparation of TEAD

An attempt to prepare TEAD according to the Mailman procedure without the large excess of dithionite did not give the material normally called TEAD. The large excess is necessary.

Preparation of a soluble dithionite: Tetrabutylammonium dithionite [TBAD]

Lattice calculations indicate that the lattice energy of TBAD would be very low (potential for ionic liquid or spontaneous formation of the monomer salt by S-S bond cleavage). One reaction was done to explore the synthesis following the Mailman procedure. On warming to RT the reaction mixture (SDT: 1.77g, 10.5 mmol; TBAC 0.286 g, 1.75 mmol; SO₂ 9.7 g) gave a clear pink solution over a white solid. Separation of the soluble materials and evaporation gave a viscous brown solid/oil (currently being characterized) no TBAC remaining in drybox (on order)

Preparation of a soluble dithionite: Silver dithionite



It was agreed that the reaction to give Ag₂S₂O₄ was worth the attempt so the reaction was attempted from two directions. There was an immediate reaction to deposit a black solid. All the reaction products were insoluble and there was a net mass loss corresponding to the loss of two equivalents of SO₂ based on the BCE above.

$\text{Ag}_2\text{S}_2\text{O}_4 \rightarrow 2 \text{Ag} + 2 \text{SO}_2$	$\text{S}_2\text{O}_4^{2-} \rightarrow 2 \text{SO}_2 + 2\text{e}^-$	$E^\circ = 0.420 \text{ V}$
	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	$E^\circ = 0.800 \text{ V}$
	NET	$E^\circ = 1.220 \text{ V}$

Something between a well trained Labrador retriever and a second year inorganic student could have predicted this reaction but in general you have to try these things out "just to be sure"

Preparation of a soluble dithionite: 18-crown-6 dithionite

According to Mincey and Traylor (1978) sodium dithionite is soluble in water and alcohols when mixed with 18-crown-6 in a 1 : 2.2 ratio. As an extension of this rather poorly described reaction the reaction of 18-crown-6 according to the Mailman procedure for TEAD was done twice.

	2 C₁₂H₂₄O₆ 18-Crown-6 FW = 264.32	+	Na₂S₂O₄ FW = 171.11	→	[C₁₂H₂₄O₆-Na]₂S₂O₄ FW = 699.75
RMS07-9	2.41g 9.1 mmol		1.69 g 9.7 mmol		2X excess dithionite
RMS07-10	4.26g 16.1 mmol		10.96 g 63.0 mmol		8X excess dithionite

Both reactions (solids mixed in SO₂) showed an immediate reaction on warming to RT to give green or yellow solutions over white insoluble solids. Stirring at RT followed by filtration and evaporation give thick red-orange oils (currently being characterized, RMS07-10 precipitating crystals from oil).

Experimental Issues on the Characterization of Soluble Dithionites

Preparation: The point is to relate to dithionite chemistry in SO₂ but it is clear that all products following the Mailman procedure initially give oils. It is possible that recrystallisation from a different non-aqueous solvent will give the crystals.

Analysis: The literature reports two methods of analysis for dithionites:

a) Uv-visible analysis using the strong 313 nm absorption ($\epsilon = 8000 \text{ M}^{-1}\text{cm}^{-1}$, but there is some disagreement on the molar absorptivity). b) chemical oxidation (essentially what we did with silver) We need a facile, quantitative method to assess the purity of the dithionites that we prepare.

NMR: Once we have solutions that have a reliable analysis for dithionite we can use Evan's method to quantitatively determine the amount of SO₂- radical in the solutions produced.

Raman: A full Raman analysis of the solutions at various temperatures and concentrations can give values for K_{eq} for comparison with literature work.

DSC: The calculated low energy conformational changes in the dianion may be revealed by solid-solid phase changes and a true melting point may reveal an ionic / paramagnetic liquid.

