

# Photochemistry, Electronic Spectra and Autoxidation Mechanism of the Sodium Sulfite System

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## ABSTRACT

Sodium sulfite (sodium sulphite) is the inorganic compound with the chemical formula  $\text{Na}_2\text{SO}_3$ . A white, water-soluble solid, it is used commercially as an antioxidant and preservative. A heptahydrate is also known but it is less useful because of its greater susceptibility toward oxidation by air. The photochemical reaction of o-iodo- and o-bromophenol in an aqueous sodium sulfite solution proceeds via both nonchain and chain mechanisms. The formation of the intermediate product, aromatic radical anion, was observed. The quantum yield of the photochemical reaction of o-iodophenol increases, when the electron donor diphenylamine is irradiated. In the photolysis of o-halophenols in organic solvents, free iodine is evolved in addition to aromatic products. The products of the photolysis of o-iodophenol in ethanol and carbon tetrachloride were identified by gas chromatography-mass spectrometry. These are phenol in the case of ethanol and a mixture of o-chlorophenol and hydroxychloro-substituted biphenyls in the case of carbon tetrachloride. The quantum yields were determined for all photochemical reactions studied. The most common method for generation of alkane sulfonic acids is the reaction of alkyl bromides with sodium sulfite—the Strecker synthesis <1995COFGT (2) 113>. This approach has been reported for the preparation of  $\beta$ -amino- $\beta$ -aryl-ethanesulfonic acids from the corresponding  $\beta$ -aminopropyl bromides and sodium sulfite in water <1997AJC523>. The interesting biological activities of  $\beta$ -aminoalkanesulfonic acids (taurine analogues) initiated synthesis of their derivatives such as hydroxysaclofen 66 <1995T11465> and  $\beta$ -aminopropanesulfonic acids 67 <1996TL7319, 2002TA1129>. A mechanism for the chiral (R) - or (S) -2-aminoalkanesulfonic acid formation by reaction of the corresponding chiral aminoalcohol methanesulfonate with sodium sulfite was proposed by Xu and involves the intermediate aziridine <2002TA1129>. Diallylamine was converted into the cis- and trans-pyrrolidinesulfonates by cyclization with sodium hydrogen sulfite in an oxygen-assisted addition which is consistent with the mechanism of addition of bisulfite to alkenes.

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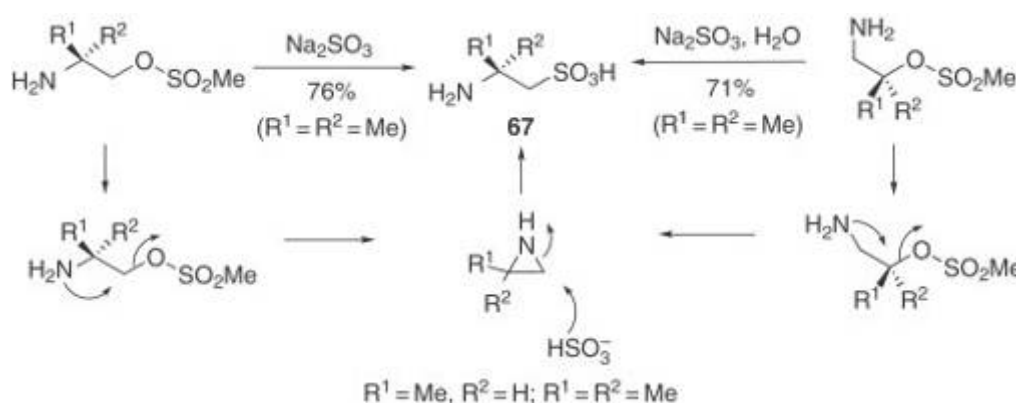


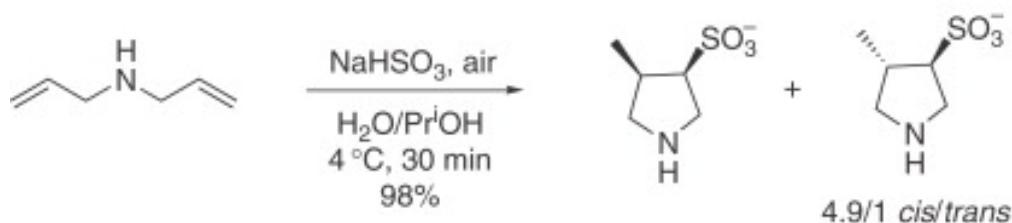
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**KEYWORDS:** photochemistry, electronic spectra, autoxidation, sodium sulfite, inorganic, reactions, mechanisms

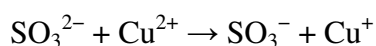




## INTRODUCTION

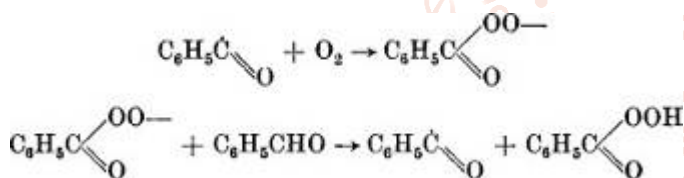
The oxidation of aqueous sodium sulphite is an auto-oxidation exemplifying the above initiation mechanisms. It is a typical chain reaction. It is very sensitive to light, the quantum yield being about  $10^5$ . It is also sensitive to the presence of some organic compounds, such as aniline, carbohydrates or glycerol; any of these, if added in small amounts, renders the sulphite solution stable to oxygen.  $\text{SO}_5^{2-}$  ion (the anion of Caro's acid) then reacts with  $\text{SO}_3^{2-}$   $\text{SO}_5^{2-} + \text{SO}_3^{2-} \rightarrow 2\text{SO}_4^{2-}$  [1,2]

The salts of some metals of variable valency accelerate the oxidation, and the oxidation only appears to proceed in the dark if traces of these metals are present. This is clearly a direct consequence of radical-ion production:



Another instance is the auto-oxidation of benzaldehyde. This is also a typical chain reaction, being susceptible to light and negative catalysts; the quantum yield is about  $10^4$

The chain mechanism below has been proposed:



This oxidation is also catalysed by suitable metallic ions, and has been the subject of detailed study for solutions in glacial acetic acid containing cobalt acetate.

Linear-sweep experiments recorded in solutions containing sodium dithionite or sulphite were discussed in sections 6.2 and 6.3 using rotating-disc electrodes.[3,4] With these electrodes, well-shaped limiting-current plateaux were obtained for the oxidation of dithionite to sulphite, while the second plateau shows some kinetic influence. [5,6] This could be explained by changes in electrode surface conditions, which inevitably have an effect on the kinetics of sulphite oxidation. Despite this disadvantage, it is still possible to measure sulphite concentrations based on the plateau currents of the second oxidation wave. Therefore, the investigation in this section is started immediately with a double potential step chronoamperometric experiment in

order to measure the limiting current  $I_{0.45V}$  of sodium dithionite oxidation at a first applied potential  $E_{\text{dit}} = +0.45V$  vs.  $\text{Ag}|\text{AgCl}$ . It will also measure the step related to the sum of sodium dithionite and sulphite oxidation ( $I_{0.8V}$ ) at a second applied potential  $E_{\text{sul}} = +0.8V$  vs.  $\text{Ag}|\text{AgCl}$  using the wall-jet electrode setup. Each potential is alternately applied for 5s, and the resulting current signal is measured at the end of each potential step.[7,8]

The variation of the limiting currents of the oxidation of sodium dithionite and sulphite is shown as a function of time during decomposition of sodium dithionite in an alkaline solution. In the oxidation of dithionite corresponding to the first potential, two electrons are exchanged, while at the second potential, six electrons are released. This means that the current contribution of sulphite ( $I_{L,\text{sul}}$ ) present in solution, also shown and can be calculated.

In another review, Oxidation of sulfite is an important process in flue gas desulfurization. The inhibitory effects of four inhibitors on the intrinsic oxidation of sulfite were compared, and ethanol was found to be an excellent inhibitor. The intrinsic oxidation kinetics of sulfite in the presence of ethanol used as an inhibitor was investigated using a batch apparatus. The reaction orders of the reagents and the activation energy were obtained. The results indicate that the intrinsic reaction proceeds in two steps: rapid reaction in an oxygen-rich state and slow reaction in an oxygen-depleted state. Integrated with the macroscopic oxidation kinetics of calcium sulfite in the presence of an ethanol inhibitor, it was concluded that the macroscopic oxidation process is controlled by the intrinsic reaction rate and the intrinsic oxidation reaction proceeds in the rapid reaction state. Furthermore, a mechanism for the intrinsic reaction is proposed based on a steady-state assumption. The results derived with this mechanism are in good agreement with the experimental results.[9,10]

Sodium sulfite is available commercially in several grades (eatalyzed SULFTECH €1, Catalyzed SULFTEeH€1 with sodium metabisulfite, reagent Aes (American Chemical Society)), with the following ranges of specifications: purity, 94.5-98.5%; sodium chloride, 0.01-0.02%; iron (Fe), 0.001--c 0.002%; arsenic 1 ppm (mg/kg); heavy metals (as lead), 0.001

%; and additives (cobalt salts ,0.01 %; anti-caking agent, 0.07%).

In petroleum technology, sulfur, most commonly as sodium sulfite, is used as an oxygen scavenger. Sulfur dioxide is used in oil refining as a selective extraction solvent in the Edeleanu process, in which aromatic components are extracted from a kerosene stream with sulfur dioxide, leaving a purified stream of saturated aliphatic hydrocarbons, which are relatively insoluble in sulfur dioxide. Sulfur dioxide acts as a cocatalyst or catalyst modifier in certain processes for oxidation of ortho-xylene or naphthalene to phthalic anhydride. [11,12]

### Discussion

Sodium sulfite is used in neutral semi-chemical pulping, in acid sulfite pulping, in high-yield sulfite cooling and in some kraft pulping processes; in the chemical industry as a reducing agent and source of sulfite ion; as an antioxidant in water treatment chemicals; in the food industry as an antioxidant and enzyme inhibitor in the processing of fruit and vegetables; in the photographic industry as a film and stain preservative during developing; in the textile industry as a bleach and antichlor; and to remove oxygen from water used in boilers,[13,14]oil-well flooding, oil-well drilling muds and other situations in which it is important to remove oxygen to reduce corrosion

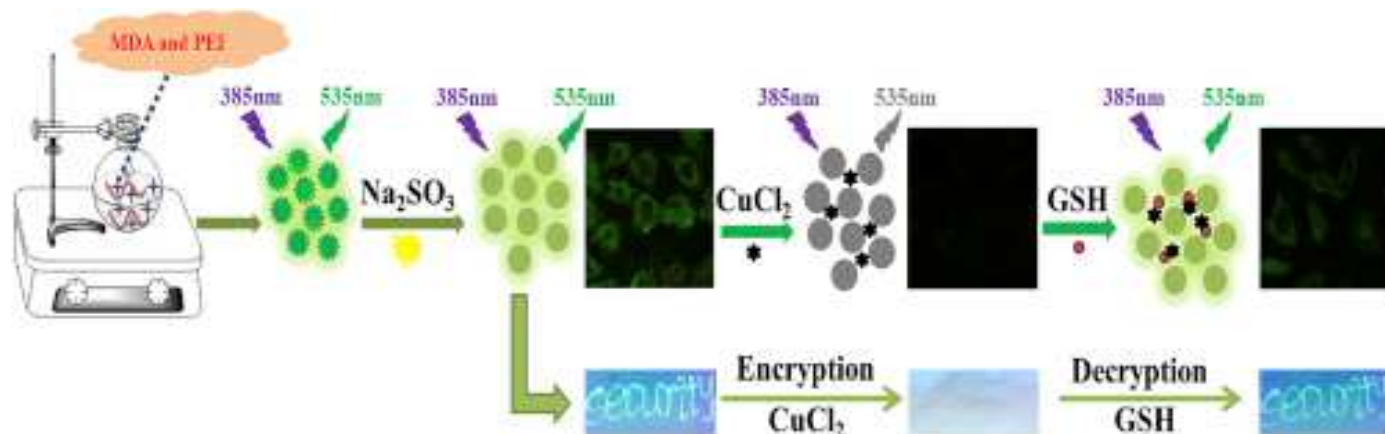
Sodium dithionite is not stable under physiological conditions, with the rate of decomposition increasing with increasing acidity. Upon contact with moisture, it is oxidized to hydrogen sulfite ( $\text{HSO}_3^-$ ), sulfite ( $\text{SO}_3^{2-}$ ) and hydrogen sulfate ( $\text{HSO}_4^-$ ), and under strongly acidic conditions it may liberate sulfur dioxide. Under anaerobic conditions (such as in the lower gastrointestinal tract), hydrogen sulfite ( $\text{HSO}_3^-$ ) and thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) may be formed. Hydrogen sulfite ( $\text{HSO}_3^-$ ) can be absorbed after ingestion. It is efficiently metabolized, and the major part rapidly excreted as sulfate into the urine.[15,16]

The oxidation of Cu (II) complexes with tetra, penta and hexaglycine in borate buffer aqueous solution, by dissolved oxygen is strongly accelerated by sulfite. The formation of Cu (III) complexes with maximum absorbances at 250 nm ( $\epsilon = 9000 \text{ mol}^{-1} \text{ L cm}^{-1}$ ) and 365 nm ( $\epsilon = 7120 \text{ mol}^{-1} \text{ L cm}^{-1}$ ) was also characterized by using rotating ring-disk voltammetry, whose anodic and cathodic components were observed in voltammograms recorded in solutions containing Cu (II). Voltammograms,

obtained at various rotation speeds, showed that the Cu (III) species electrochemically generated is not stable over the entire time window of the experiment and in solutions containing tetraglycine the overall limiting current is controlled by the kinetics of an equilibrium involving Cu (II) species. The calculated first order rate constant of the decomposition was  $4.37 \times 10^{-3} \text{ s}^{-1}$ . Electrochemical experiments carried out in Cu (II) solutions after the addition of relatively small amounts of sulfite demonstrated that the Cu (III) species formed in the chemical reaction is the same as the one collected at the ring electrode when Cu (II) is oxidized at the disk electrode in ring-disk voltammetry. The concentration of Cu (III) complexes is proportional to the amount of added sulfite and the results indicated that indirect analytical methods for sulfite may be developed by means of spectrophotometric or amperometric detection of the chemically generated product.[17,18]

Fluorescent organic nanoparticles (FONs) play important roles in the monitoring and controls of biological systems. To fulfill such duties, we have to investigate how the nanoplatforms interact with living matters. Currently, very limited information concerning the potential risks and toxicity has been reported for FONs except the MTT assay. In this contribution, the amine-rich cationic precursor (polyethyleneimine) initiates one-pot copolymerization with methyl dopa sesquihydrate and water-soluble fluorescent nanoparticles are afforded. The influence of reduction agent (sodium sulfite) on the luminescence, microstructure and crystallinity has been discussed and the corresponding stabilities are substantially improved. Further studies reveal that selective  $\text{Cu}^{2+}$  detection has been realized due to “on-off” change and the limit of detection is determined to be 52 nM. It has been discovered that glutathione (GSH) can recover its green luminescence in terms of strong affinity of GSH to copper ions. For the first time, three different cell viability experiments including MTS assay, Annexin V-APC/7-AAD kit and double stain technique have been performed to support the negligible cytotoxicity of FONs in living cells. Spectra imaging has been employed for the identification of  $\text{Cu}^{2+}$  and GSH in HeLa cells. In addition, the  $\text{Cu}^{2+}$ -GSH pairs can generate an “AND” logic gate during recognition sequence operations. It will be the first example that the effectiveness of encryption and decryption has been verified via  $\text{Cu}^{2+}$  and GSH based on FONs.[19,20]





The electrochemiluminescence (ECL) of  $Tb^{3+}$ -enoxacin- $Na_2SO_3$  system (ENX system) and  $Tb^{3+}$ -ofloxacin- $Na_2SO_3$  system (OFLX system) in aqueous solution is reported. ECL is generated by the oxidation of  $Na_2SO_3$ , which is enhanced by  $Tb^{3+}$ -fluoroquinolone (FQ) complex. The ECL intensity peak versus potential corresponds to oxidation of  $Na_2SO_3$ , and the ECL emission spectra (the peaks are at 490, 545, 585 and 620 nm) match the characteristic emission spectrum of  $Tb^{3+}$ , indicating that the emission is from the excited state of  $Tb^{3+}$ . The mechanism of ECL is proposed and the difference of ECL intensity between ENX system and OFLX system is explained. Conditions for ECL emission were optimized. The linear range of ECL intensity versus concentrations of pharmaceuticals is  $2.0 \times 10^{-10}$ – $8.0 \times 10^{-7}$  mol l<sup>-1</sup> for ENX and  $6.0 \times 10^{-10}$ – $6.0 \times 10^{-7}$  mol l<sup>-1</sup> for OFLX, respectively. A theoretical limit of detection is  $5.4 \times 10^{-11}$  mol l<sup>-1</sup> for ENX and  $1.6 \times 10^{-10}$  mol l<sup>-1</sup> for OFLX, respectively. The ECL was satisfactorily applied to the determination of the two FQs in dosage form and urine sample.[21,22]

The objective of another review seen was to determine the effect of (bi) sulfite (hydrated sulfur dioxide) on human neutrophils and the ability of these immune cells to produce reactive free radicals due to (bi) sulfite oxidation. Myeloperoxidase (MPO) is an abundant heme protein in neutrophils that catalyzes the formation of cytotoxic oxidants implicated in asthma and inflammatory disorders. In this study sulfite ( $\bullet$ )  $SO_3^-$  and sulfate ( $\bullet$ -) anion radicals are characterized with the ESR spin-trapping technique using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) in the reaction of (bi) sulfite oxidation by human MPO and human neutrophils via sulfite radical chain reaction chemistry. After treatment with (bi) sulfite, phorbol 12-myristate 13-acetate-stimulated neutrophils produced DMPO-sulfite anion radical, -superoxide, and -hydroxyl radical adducts. The last adduct probably resulted, in part, from the conversion of DMPO-sulfate to DMPO-hydroxyl radical adduct via a nucleophilic substitution reaction

of the radical adduct. This anion radical ( $SO_3^{\bullet-}$ ) is highly reactive and, presumably, can oxidize target proteins to protein radicals, thereby initiating protein oxidation. Therefore, we propose that the potential toxicity of (bi) sulfite during pulmonary inflammation or lung-associated diseases such as asthma may be related to free radical formation.[23,24]

Another review compared 3 commonly used quenching agents for dechlorinating samples prior to disinfection byproduct (DBP) analysis under typical drinking water sampling conditions for a representative suite of chlorination byproducts. Ascorbic acid and sodium sulfite quenched the residual free chlorine to below detection within 5 seconds. Ammonium chloride did not quench the chlorine to below detection with up to a 70% molar excess, which agrees with published ammonium chloride-chlorine chemistry.

With respect to the DBPs, ascorbic acid worked well for the trihalomethanes and haloacetic acids, except for dibromiodomethane, which exhibited 2.6–28% error when using ascorbic acid compared to non-quenched control samples. Sodium sulfite also worked well for the trihalomethanes (and performed similarly to ascorbic acid for dibromiodomethane) and was the best performing quenching agent for MX and the inorganic DBPs, but contributed to the decay of several emerging DBPs, including several halonitromethanes and haloacetamides. Ammonium chloride led to considerable errors for many DBPs, including 27–31% errors in chloroform concentrations after 24 hours of storage. This work shows that ascorbic acid is suitable for many of the organic DBPs analyzed by gas chromatography-electron capture detection and that sodium sulfite may be used for simultaneous chlorite, chlorate, and bromate analysis.[25,26]

## Results

Sodium Sulfite, Ammonium Sulfite, Sodium Bisulfite, Potassium Bisulfite, Ammonium Bisulfite, Sodium Metabisulfite, and Potassium Metabisulfite are inorganic salts that function as reducing agents in

cosmetic formulations. All except Sodium Metabisulfite also function as hair-waving/straightening agents. In addition, Sodium Sulfite, Potassium Sulfite, Sodium Bisulfite, and Sodium Metabisulfite function as antioxidants. Although Ammonium Sulfite is not in current use, the others are widely used in hair care products. Sulfites that enter mammals via ingestion, inhalation, or injection are metabolized by sulfite oxidase to sulfate. In oral-dose animal toxicity studies, hyperplastic changes in the gastric mucosa were the most common findings at high doses. Ammonium Sulfite aerosol had an acute LC (50) of >400 mg/m (3) in guinea pigs. A single exposure to low concentrations of a Sodium Sulfite fine aerosol produced dose-related changes in the lung capacity parameters of guinea pigs. A 3-day exposure of rats to a Sodium Sulfite fine aerosol produced mild pulmonary edema and irritation of the tracheal epithelium. Severe epithelial changes were observed in dogs exposed for 290 days to 1 mg/m (3) of a Sodium Metabisulfite fine aerosol. These fine aerosols contained fine respirable particle sizes that are not found in cosmetic aerosols or pump sprays. None of the cosmetic product types, however, in which these ingredients are used are aerosolized. Sodium Bisulfite (tested at 38%) and Sodium Metabisulfite (undiluted) were not irritants to rabbits following occlusive exposures. Sodium Metabisulfite (tested at 50%) was irritating to guinea pigs following repeated exposure. In rats, Sodium Sulfite heptahydrate at large doses (up to 3.3 g/kg) produced fetal toxicity but not teratogenicity. [27,28]

### Conclusion

The role of depressants, which are either inorganic salts, such as sodium silicate, sodium sulfite or organic compounds such as polysaccharides, dextrin and starch derivatives, guar gums, carboxymethylcellulose and alginates, is to reduce the collection of unwanted gangue which consists of typically talcaceous or other oxide minerals.[29] This is done by either enhancing the hydrophilic nature of the gangue surface, by preventing the formation of hydrophobic species which might adsorb on the gangue surface or by preventing the coating of unwanted slimes on the mineral surface. Mechanisms of depression also include the formation of large aggregates and the complexation of the collector in solution.[30]

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