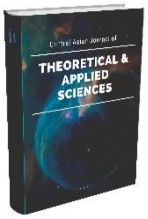

CENTRAL ASIAN JOURNAL OF THEORETICAL AND APPLIED SCIENCES

Volume: 04 Issue: 05 | May 2023 ISSN: 2660-5317
https://cajotas.centralasianstudies.org

Cobalt Catalysed Autoxidation of Dissolved Sulfur Dioxide in the Atmospheric Aqueous Phase

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Received 4th Mar 2023, Accepted 6th Apr 2023, Online 30th May 2023

Abstract: *Catalytic oxidation are processes that rely on catalysts to introduce oxygen into organic and inorganic compounds. Many applications, including the focus of this article, involve oxidation by oxygen. Such processes are conducted on a large scale for the remediation of pollutants, production of valuable chemicals, and the production of energy.[1] The common mechanism is a free radical chain reaction, where the addition of oxygen gives rise to hydroperoxides and their associated peroxy radicals (ROO•).[5] Typically, an induction period is seen at the start where there is little activity; this is followed by a gradually accelerating take-up of oxygen, giving an autocatalytic reaction which can only be kept in check by the use of antioxidants. Unsaturated compounds are the most strongly effected but many organic materials will oxidise in this way given time. Sulfur dioxide (IUPAC-recommended spelling) or sulphur dioxide (traditional Commonwealth English) is the chemical compound with the formula SO2. It is a toxic gas responsible for the odor of burnt matches. It is released naturally by volcanic activity and is produced as a by-product of copper extraction and the burning of sulfur-bearing fossil fuels.[8].*

Keywords: *cobalt, autoxidation, sulphur dioxide, atmospheric aqueous phase, free radical, antioxidants, catalysts.*

Introduction

Sulfur dioxide is one of the few common acidic yet reducing gases. It turns moist litmus pink (being acidic), then white (due to its bleaching effect). It may be identified by bubbling it through a dichromate solution, turning the solution from orange to green (Cr^{3+} (aq)). It can also reduce ferric ions to ferrous.[20]

Sulfur dioxide can react with certain 1,3-dienes in a cheletropic reaction to form cyclic sulfones. This reaction is exploited on an industrial scale for the synthesis of sulfolane, which is an important solvent in the petrochemical industry.[1]

Sulfur dioxide can bind to metal ions as a ligand to form metal sulfur dioxide complexes, typically where the transition metal is in oxidation state 0 or +1. Many different bonding modes (geometries) are recognized, but in most cases, the ligand is monodentate, attached to the metal through sulfur, which can be either planar and pyramidal η^1.[8] As a η^1-SO_2 (S-bonded planar) ligand sulfur dioxide functions as a Lewis base using the lone pair on S. SO_2 functions as a Lewis acids in its η^1-SO_2 ^{2}(S-bonded pyramidal) bonding mode with metals and in its 1:1 adducts with Lewis bases such as dimethylacetamide and trimethyl amine. When bonding to Lewis bases the acid parameters of SO_2 are $E_A = 0.51$ and $E_A = 1.56$.[3]

Sulfur dioxide is also a good reductant. In the presence of water, sulfur dioxide is able to decolorize substances. Specifically, it is a useful reducing bleach for papers and delicate materials such as clothes. This bleaching effect normally does not last very long. Oxygen in the atmosphere reoxidizes the reduced dyes, restoring the color. In municipal wastewater treatment, sulfur dioxide is used to treat chlorinated wastewater prior to release. Sulfur dioxide reduces free and combined chlorine to chloride.[30]

Sulfur dioxide is fairly soluble in water, and by both IR and Raman spectroscopy; the hypothetical sulfurous acid, H_2SO_3, is not present to any extent. However, such solutions do show spectra of the hydrogen sulfite ion, HSO_3^-, by reaction with water, and it is in fact the actual reducing agent present:[4]

$$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+$$

Sulfur dioxide is a major air pollutant and has significant impacts upon human health.[43] In addition, the concentration of sulfur dioxide in the atmosphere can influence the habitat suitability for plant communities, as well as animal life.[44] Sulfur dioxide emissions are a precursor to acid rain and atmospheric particulates. Due largely to the US EPA's Acid Rain Program, the U.S. has had a 33% decrease in emissions between 1983 and 2002. This improvement resulted in part from flue-gas desulfurization, a technology that enables SO_2 to be chemically bound in power plants burning sulfur-containing coal or oil. In particular, calcium oxide (lime) reacts with sulfur dioxide to form calcium sulfite:[5]

$$CaO + SO_2 \rightarrow CaSO_3$$

Aerobic oxidation of the $CaSO_3$ gives $CaSO_4$, anhydrite. Most gypsum sold in Europe comes from flue-gas desulfurization.[23]

To control sulfur emissions, dozens of methods with relatively high efficiencies have been developed for fitting of coal-fired power plants.[45]

Sulfur can be removed from coal during burning by using limestone as a bed material in fluidized bed combustion.[46]

Sulfur can also be removed from fuels before burning, preventing formation of SO_2 when the fuel is burnt. The Claus process is used in refineries to produce sulfur as a byproduct. The Stretford process has also been used to remove sulfur from fuel. Redox processes using iron oxides can also be used, for example, Lo-Cat[47] or Sulferox.[48]

An analysis found that 18 coal-fired power stations in the western Balkans emitted two-and-half times more sulphur dioxide than all 221 coal plants in the EU combined.[49]

Fuel additives such as calcium additives and magnesium carboxylate may be used in marine engines to lower the emission of sulfur dioxide gases into the atmosphere.[50]

As of 2006, China was the world's largest sulfur dioxide polluter, with 2005 emissions estimated to be 25,490,000 short tons (23.1 Mt). This amount represents a 27% increase since 2000, and is roughly comparable with U.S. emissions in 1980.[51]

Discussion

Oxidation catalysis is conducted by both heterogeneous catalysis and homogeneous catalysis. In the heterogeneous processes, gaseous substrate and oxygen (or air) are passed over solid catalysts. Typical catalysts are platinum, and redox-active oxides of iron, vanadium, and molybdenum. In many cases, catalysts are modified with a host of additives or promoters that enhance rates or selectivities.[34]

Important homogeneous catalysts for the oxidation of organic compounds are carboxylates of cobalt, iron, and manganese. To confer good solubility in the organic solvent, these catalysts are often derived from naphthenic acids and ethylhexanoic acid, which are highly lipophilic. These catalysts initiate radical chain reactions, autoxidation that produce organic radicals that combine with oxygen to give hydroperoxide intermediates. Generally the selectivity of oxidation is determined by bond energies. For example, benzylic C-H bonds are replaced by oxygen faster than aromatic C-H bonds.[2]

Catalytic oxidations are common in biology, especially since aerobic life subsists on energy obtained by oxidation of organic compounds by air. In contrast to the industrial processes, which are optimized for producing chemical compounds, energy-producing biological oxidations are optimized to produce energy. Many metalloenzymes mediate these reactions. The foremost challenge in catalytic oxidation is the conversion of methane to methanol. Most methane is stranded, i.e. not located near metropolitan areas. Consequently, it is flared (converted to carbon dioxide). One challenge is that methanol is more easily oxidized than is methane.[3]

Catalytic oxidation with oxygen or air is a major application of green chemistry. There are however many oxidations that cannot be achieved so straightforwardly. The conversion of propylene to propylene oxide is typically effected using hydrogen peroxide, not oxygen or air.

Under normal conditions, sulfur hydrolyzes very slowly to mainly form hydrogen sulfide and sulfuric acid:[39]

$\frac{1}{2} S_8 + 4 H_2O \rightarrow 3 H_2S + H_2SO_4$

The reaction involves adsorption of protons onto S_8 clusters, followed by disproportionation into the reaction products.[13]

The second, fourth and sixth ionization energies of sulfur are 2252 kJ/mol^{-1}, 4556 kJ/mol^{-1} and 8495.8 kJ/mol^{-1},respectively. A composition of products of sulfur's reactions with oxidants (and its oxidation state) depends on that whether releasing out of a reaction energy overcomes these thresholds. Applying catalysts and / or supply of outer energy may vary sulfur's oxidation state and a composition of reaction products. While reaction between sulfur and oxygen at normal conditions gives sulfur dioxide (oxidation state +4), formation of sulfur trioxide (oxidation state +6) requires temperature 400 – 600 °C and presence of a catalyst.[25]

In reactions with elements of lesser electronegativity, it reacts as an oxidant and forms sulfides, where it has oxidation state –2.

Sulfur reacts with nearly all other elements with the exception of the noble gases, even with the notoriously unreactive metal iridium (yielding iridium disulfide).[14] Some of those reactions need elevated temperatures.[15]

Results

Sulfur has 23 known isotopes, four of which are stable: ^{32}S (94.99%±0.26%), ^{33}S (0.75%±0.02%), ^{34}S (4.25%±0.24%), and ^{36}S (0.01%±0.01%).[21][22] Other than ^{35}S, with a half-life of 87 days, the radioactive isotopes of sulfur have half-lives less than 3 hours.

The preponderance of sulfur-32 is explained by its production in the so-called alpha-process (one of the main classes of nuclear fusion reactions) in exploding stars. Other stable sulfur isotopes are produced in the bypass processes related with argon-34, and their composition depends on a type of a stellar explosion. For example, there is more sulfur-33 come from novae, than from supernovae.[23]

On the planet Earth the sulfur isotopic composition was determined by the Sun. Though it is assumed that the distribution of different sulfur isotopes should be more of less equal, it has been found that proportions of two most abundant sulfur isotopes sulfur-32 and sulfur-34 varies in different samples. Assaying of these isotopes ratio (δ34S) in the samples allows to make suggestions about their chemical history, and with support of other methods, it allows to age-date the samples, estimate temperature of equilibrium between ore and water, determine pH and oxygen fugacity, identify the activity of sulfate-reducing bacteria in the time of formation of the sample, or suggest the main sources of sulfur in ecosystems.[24] However, discussions about what is the real reason of the δ34S shifts, biological activity or postdepositional alteration, go on.[25]

For example, when sulfide minerals are precipitated, isotopic equilibration among solids and liquid may cause small differences in the $\delta^{34}S$ values of co-genetic minerals. The differences between minerals can be used to estimate the temperature of equilibration. The $\delta^{13}C$ and $\delta^{34}S$ of coexisting carbonate minerals and sulfides can be used to determine the pH and oxygen fugacity of the ore-bearing fluid during ore formation.44

Scientists measure the sulfur isotopes of minerals in rocks and sediments to study the redox conditions in the oceans in the past. Sulfate-reducing bacteria in marine sediment fractionate sulfur isotopes as they take in sulfate and produce sulfide. Prior to 2010s, it was thought that sulfate reduction could fractionate sulfur isotopes up to 46 permil[26] and fractionation larger than 46 permil recorded in sediments must be due to disproportionation of sulfur compounds in the sediment. This view has changed since the 2010s as experiments show that sulfate-reducing bacteria can fractionation to 66 permil.[27] As substrates for disproportionation are limited by the product of sulfate reduction, the isotopic effect of disproportionation should be less than 16 permil in most sedimentary settings.[28]

In most forest ecosystems, sulfate is derived mostly from the atmosphere; weathering of ore minerals and evaporites contribute some sulfur. Sulfur with a distinctive isotopic composition has been used to identify pollution sources, and enriched sulfur has been added as a tracer in hydrologic studies. Differences in the natural abundances can be used in systems where there is sufficient variation in the ^{34}S of ecosystem components. Rocky Mountain lakes thought to be dominated by atmospheric sources of sulfate have been found to have characteristic ^{34}S values from lakes believed to be dominated by watershed sources of sulfate.54

The radioactive sulfur-35 is formed in cosmic ray spallation of the atmospheric ^{40}Ar. This fact may be used for proving the presence of recent (not more than 1 year) atmospheric sediments in various things. This isotope may be obtained artificially by different ways. In practice, the reaction $^{35}Cl + n \rightarrow {}^{35}S + p$ is used by irradiating potassium chloride with neutrons.[29] The isotope sulfur-35 is used in various sulfur-containing compounds as a radioactive tracer for many biological studies, for example, the Hershey-Chase experiment.

Because of its weak beta activity, S-35 compounds are relatively safe as long as they are not ingested or absorbed by the body.[30]

Sulfur polycations, S_8^{2+}, S_4^{2+} and S_{16}^{2+} are produced when sulfur is reacted with oxidising agents in a strongly acidic solution.[40] The colored solutions produced by dissolving sulfur in oleum were first reported as early as 1804 by C.F. Bucholz, but the cause of the color and the structure of the polycations involved was only determined in the late 1960s. S_8^{2+} is deep blue, S_4^{2+} is yellow and S_{16}^{2+} is red.[12]

Reduction of sulfur gives various polysulfides with the formula S_x^{2-}, many of which have been obtained crystalline form. Illustrative is the production of sodium tetrasulfide:

$4 Na + S_8 \rightarrow 2 Na_2S_4$

Some of these dianions dissociate to give radical anions, such as S_3^{-} gives the blue color of the rock lapis lazuli.[55]

This reaction highlights a distinctive property of sulfur: its ability to catenate (bind to itself by formation of chains). Protonation of these polysulfide anions produces the polysulfanes, H_2S_x where x= 2, 3, and 4.[42] Ultimately, reduction of sulfur produces sulfide salts:

$16 Na + S_8 \rightarrow 8 Na_2S$

The interconversion of these species is exploited in the sodium–sulfur battery.[56]

Conclusions

In the 1880s, while studying Beggiatoa (a bacterium living in a sulfur rich environment), Sergei Winogradsky found that it oxidized hydrogen sulfide (H_2S) as an energy source, forming intracellular sulfur droplets. Winogradsky referred to this form of metabolism as inorgoxidation (oxidation of inorganic compounds).[96] Another contributor, who continued to study it was Selman Waksman.[97] Primitive bacteria that live around deep ocean volcanic vents oxidize hydrogen sulfide for their nutrition, as discovered by Robert Ballard.[8]

Sulfur oxidizers can use as energy sources reduced sulfur compounds, including hydrogen sulfide, elemental sulfur, sulfite, thiosulfate, and various polythionates (e.g., tetrathionate).[98] They depend on enzymes such as sulfur oxygenase and sulfite oxidase to oxidize sulfur to sulfate. Some lithotrophs can even use the energy contained in sulfur compounds to produce sugars, a process known as chemosynthesis. [49] Some bacteria and archaea use hydrogen sulfide in place of water as the electron donor in chemosynthesis, a process similar to photosynthesis that produces sugars and uses oxygen as the electron acceptor. Sulfur-based chemosynthesis may be simplifiedly compared with photosynthesis:[50]

$H_2S + CO_2 \rightarrow \text{sugars} + S$

$H_2O + CO_2 \rightarrow \text{sugars} + O_2$

There are bacteria combining these two ways of nutrition: green sulfur bacteria and purple sulfur bacteria.[99] Also sulfur-oxidizing bacteria can go into symbiosis with larger organisms, enabling the later to use hydrogen sulfide as food to be oxidized. Example: the giant tube worm.[100]

There are sulfate-reducing bacteria, that, by contrast, "breathe sulfate" instead of oxygen. They use organic compounds or molecular hydrogen as the energy source.[99] They use sulfur as the electron acceptor, and reduce various oxidized sulfur compounds back into sulfide, often into hydrogen sulfide. They can grow on other partially oxidized sulfur compounds (e.g. thiosulfates, thionates, polysulfides, sulfites).[54]

There are studies pointing that many deposits of native sulfur in places that were the bottom of the ancient oceans have biological origin.[101][102][103] These studies indicate that this native sulfur have been obtained through biological activity, but what is responsible for that (sulfur-oxidizing bacteria or sulfate-reducing bacteria) is still unknown for sure.

Sulfur is absorbed by plants roots from soil as sulfate and transported as a phosphate ester. Sulfate is reduced to sulfide via sulfite before it is incorporated into cysteine and other organosulfur compounds.[104]

$SO_4^{2-} \rightarrow SO_3^{2-} \rightarrow H_2S \rightarrow$ cysteine (thiol) → methionine (thioether)

While the plants' role in transferring sulfur to animals by food chains is more or less understood, the role of sulfur bacteria is just getting investigated[103]

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