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ORIGINAL CONTRIBUTION

Aspects of different kind of thiol molecules and thiyl radical species

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ABSTRACT

The study of cobalt-superoxo complexes has garnered significant attention due to their relevance to various biochemical processes and the elucidation of fundamental oxygen activation chemistry. This research focuses on exploring the reactions of cobalt-superoxo complexes to uncover insights into their roles in metabolic pathways and their potential applications in biomimetic systems. Specifically, the investigation aims to address several key objectives: understanding the participation of superoxo radical species in metabolic processes, examining disproportionation reactions in systems featuring substitution-labile transition metal centers akin to superoxide dismutase action, exploring the redox behavior of compounds containing superoxo bridges as oxygen carriers, and elucidating the mechanisms of dioxygen activation by metal complexes. By delving into these reactions and behaviors, researchers seek to enhance our understanding of metalloproteins' functions and the broader implications for biological systems. This study contributes to advancing knowledge in bioinorganic chemistry and sheds light on the intricate interplay between metal complexes and biological processes.

KEY WORDS: Predator-prey, Eco-epidemiology, Infection, Stability, Hopf-bifurcation

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1. INTRODUCTION

Because they react with free radicals, bio-thiols are remarkably effective antioxidants that shield living cells from the damaging effects of these radicals. Thiols undergo one electron oxidation during these antioxidant processes, producing thiyl radicals as a byproduct. Because of this, interest has mostly been drawn to thiols' antioxidant qualities. The thiyl radicals (RS•) that are concurrently generated in these reactions have received comparatively less attention. However, the ability of thiols to detoxify free radicals is not the only factor that determines their ability to be protective and reparative; the thiyl radical's chemical makeup and reactivity also play a role. Moreover, prompt and effective elimination of the RS• radical disrupts the equilibrium of the antioxidant process, hence enhancing the ability to repair. Risky thiyl radicals that have the potential to induce peroxidative damage should be reduced to thiols via regenerative reduction right away. Under normal circumstances, thiyl radicals can react with thiolate anion to produce an intermediate disulfide radical anion (RSSR•), which can then react to produce superoxide radical anion (O2•-), which is then inactivated by a process that is catalysed by superoxide dismutase (SOD). By interacting with ascorbate to create a low-activity ascorbyl radical that then enters the disproportiation reaction, thiyl radicals can also be reduced to thiols.

An antioxidant is a material that, although it exists in very small quantities relative to the substrate, has the ability to shield oxidation-sensitive substrates from peroxidative damage. All substances that avert peroxidative damage to cellular lipids, proteins, and nucleic acids at low concentrations are considered biological antioxidants. Among these substances, bio-thiols are important for biological processes because of their potent reductive activity and ability to interact with free radicals.

1.2. Types and formation of reactive oxygen species:

Free radicals are atoms or groups of atoms bearing one or more unpaired electrons causing damages to tissues and organs leading to different pathological states [1]. Reactive oxygen species (ROS) (Fig. 1) include hydroxyl radicals (•OH), superoxide radical anion (O2•-) and hydroperoxyl radical HO2• (a form with proton addition), and also the non-radical species: hydrogen peroxide (H2O2) and singlet oxygen 1O2..

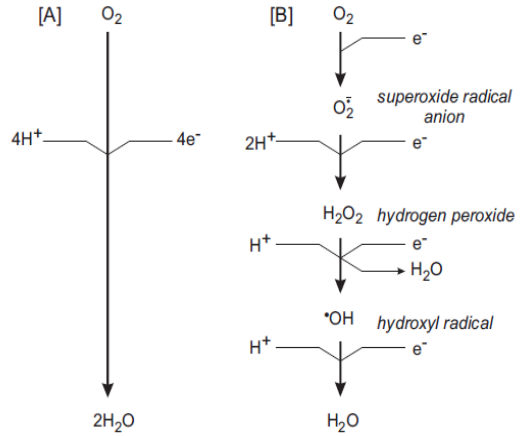


Fig. 1: Reduction of molecular oxygen to water (A) and successive one-electron reduction yielding reactive oxygen species ROS (B)

In the course of the most of the biological reactions, O2•- is formed which is transformed to H2O2 spontaneously or in enzymatic reactions catalyzed by superoxide dismutase (SOD) (reaction 1):

$$O_2^{\bullet} + O_2^{\bullet} + 2H^{+} \xrightarrow[\text{or}]{\text{SOD}} O_2 + H_2O_2 \qquad (1)$$
(Spontaneous)

H2O2 does not elicit direct strong oxidative action, but it can easily permeate across plasma membranes and oxidize transition metal ions (Fe+2, Cu+1), which results in the formation of reactive hydroxyl radical •OH at different places within cell (reaction 2):

$$H_2O_2 + Fe^{2+} \longrightarrow {}^{\bullet}OH + OH^{-} + Fe^{3+} \qquad (2)$$

Superoxide radical anion can participate in repeated reduction of Fe+3 and regeneration of Fe+2 (reaction 3):

$$O_2^{-} + Fe^{3+} \longrightarrow O_2 + Fe^{2+} \qquad (3)$$

Combining the equations 2 and 3, we obtain reaction 4, called biological Fenton reaction:

$$O_2^{\cdot-} + H_2O_2 \xrightarrow{Fe^{2+}/Fe^{3+}} {}^{\bullet}OH + OH^- + O_2 \qquad (4)$$

Therefore, in the presence of transition metals, appearance of one type of ROS in the cell creates the possibility of formation of the remaining ROS.

1.3 Oxidative stress in living cells:

A characteristic feature of ROS is their exceptional reactivity caused by the tendency to gain stability by pairing with an electron. Thus, under certain circumstances electron(s) can be abstracted from some biologically important molecules, such as proteins, nucleic acids and lipids under the influence of free radicals. Lipids, the components of cell membranes, are particularly vulnerable to such attack. Electron abstraction from these molecules initiates free radical chain reaction, involving oxidation of fatty acids with the creation of peroxides, which is called lipid peroxidation [2]. This process starts with H atom abstraction under the influence of •OH radical to form alkyl radical L• (reaction 5). Lipid peroxide radicals (L-OO•) are formed next (reaction 6), and they can abstract H atoms from other molecules with production of lipid peroxides (LOOH) (reaction 7). L-OO• can also react with lipid membrane and cytoplasmic proteins: Cyclic, multiple repetition of reactions 6 and 7 corresponds to prolongation stage, which can be stopped by reactions between two free radicals with the formation of products, which are not free radicals any more, that is called termination stage (reactions 8–10):

$$LH \xrightarrow{{}^{\bullet}OH \;\; H_2O} L^{\cdot} \qquad (5)$$

$$L^{\cdot} + O_2 \longrightarrow L\text{-}OO^{\cdot} \qquad (6)$$

$$LH + L\text{-}OO^{\cdot} \longrightarrow L\text{-}OOH + L^{\cdot} \qquad (7)$$

$$L^{\cdot} + L^{\cdot} \longrightarrow L\text{-}L \qquad (8)$$

$$L\text{-}OO^{\cdot} + L\text{-}OO^{\cdot} \longrightarrow L{=}O + L\text{-}OH + O_2 \qquad (9)$$

$$L\text{-}OO^{\cdot} + L^{\cdot} \longrightarrow L{=}O + L\text{-}OH \qquad (10)$$

The enhanced peroxidation of membrane lipids leads to the introduction of polar peroxidic, carbonyl and hydroxyl groups into their molecules, which markedly diminishes their hydrophobicity and induces formation of toxic aldehydes and hydrocarbons. Not only lipids but also proteins and nucleic acids [3] can be subjected to peroxidation which, however, is not a cascade reaction. Protein molecules not so easily exchange unpaired electron, but rather they react with ascorbate or glutathione, thereby contributing to a decrease in cellular pool of low molecular weight redox buffers.

$$R\text{-}H + {}^{\bullet}OH \longrightarrow R^{\bullet} + H_2O$$

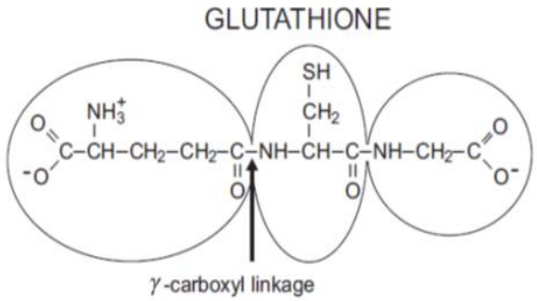
$$R^{\bullet} + O_2 \longrightarrow R\text{-}OO^{\bullet}$$

ROS are continuously generated during oxygen metabolism, but also momentarily neutralized by complex antioxidant system (so called ROS scavengers). Therefore, physiological level of ROS remains under very strict control. Danger appears only when a balance between pro- and antioxidants is disturbed, i.e. when capabilities of the cells detoxicant is outreached. Adverse ROS effects can be overcome by two independent mechanisms. The first one (and the most important) makes use of the enzymes, such as catalase, glutathione peroxidise and SOD, providing protection against Fenton reaction. The second mechanism is nonenzymatic and involves the action of reductive substances (antioxidants) in the cells, such as ascorbic acid, tocopherol,

carotene, uric acid, and thiol compounds: glutathione and lipoic acid.

1.4 Thiols as biological antioxidant systems:

Both, intracellular and extracellular redox states of thiols, play a critical role in the determination of protein structure and function, regulation of enzymatic activity, control of the activity of transcription factors and antioxidant protection [4]. Antioxidant properties of thiol compounds depend on different mechanisms. These compounds can act as thiol/disulfide component of redox buffer, free radical scavengers and chelators of metal ions.



Biological action of cellular thiol compounds, such as glutathione (GSH), is related to the activity of hydrosulfide group which determines their ability to participate in antioxidant and detoxicant reactions [5].

As a thiol compound, glutathione fulfils a very important role of an antioxidant in the cells. GSH is relatively "resistant" to spontaneous oxidation, can enter a non-enzymatic reaction with hydroxyl radical (•OH) (cytotoxic product of Fenton reaction), and react with NO3–, ONOO–, O2 and O2•-.

Glutathione plays a significant role in detoxification of H2O2 and organic peroxides created during lipid peroxidation, in which glutathione peroxidise and glutathione reductase are engaged (Fig. 2). In antioxidant reactions, the reduced GSH is oxidized yielding disulfide (oxidized glutathione), that can be again reduced to thiol with the participation of glutathione reductase and NADPH. These reactions constitute an important redox cycle in the cells. When the peroxidative processes remain at physiological level, and at sufficient availability of NADPH and activity of glutathione reductase, high physiological GSH/GSSG ratio is maintained in normal range.

Antioxidant role of GSH consists also in its ability to react with organic free radicals (e.g. proteins and other molecules), which enables it to participate in regeneration of the damaged molecules.

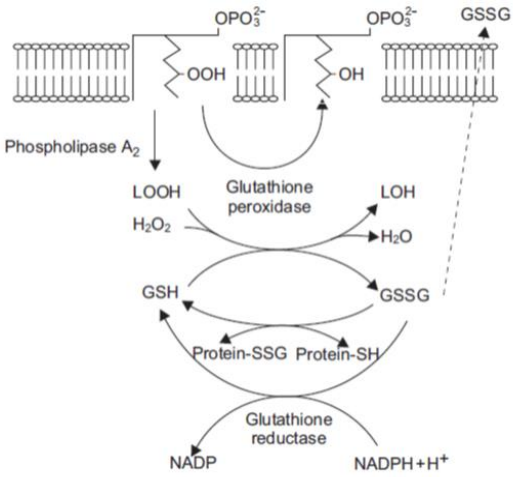
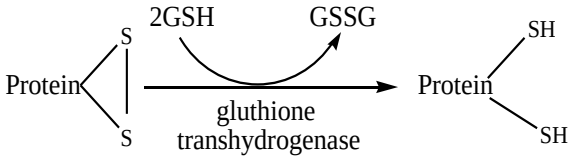


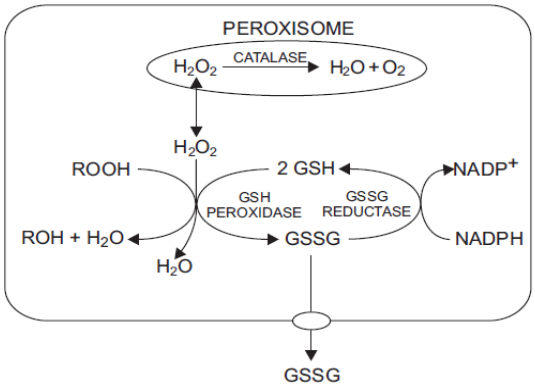
Fig. 2: Oxidation and reduction of glutathione by the enzymatic pathways.

In addition, –SH group plays an important antioxidant role by reducing disulfide bridges to free –SH groups. These reactions involving GSH can be nonenzymatic, but they are considerably accelerated by glutathione transhydrogenases (thiotransferases).



H2O2 formed in the cells independently of glutathione peroxidase activity can also be reduced by catalases present in peroxisomes (Fig. 3), while glutathione peroxidase function is particularly important in mitochondria, where catalases are absent. Therefore, mitochondrial GSH

plays a critical role in protection against ROS formed in this structure. Strong oxidative and nitrosylative stress quickly and efficiently diminishes GSH level in the cells. Hence, aggravation of per oxidative injury and NADPH deficit (due to decreased activity of glucose-6-phosphate dehydrogenase) leads to the accumulation of glutathione disulfide (GSSG). Oxidized glutathione (GSSG) is not only a useless metabolite but it is also highly dangerous to the cells. The increased GSSG level facilitates formation of mixed disulfides, i.e. protein



glutathionylation, which induces changes in redox status of thiols. Consequently, it affects so important biological processes in the cells as regulation of gene transcription, activity of enzymes and receptors. Another mechanism protecting the cells against GSSG excess involves its translocation outside the cells which, however, leads to a drop in intracellular glutathione pool.

Fig. 3: Hydrogen peroxide biodegradation by GSH peroxidise in the cytosol and by catalase in peroxisome.

1.5 Biologically Important Thiols in Various Vegetables and Fruits:

Nutritional practices and the onset of many chronic illnesses (such as diabetes, Alzheimer's, and cancer) are strongly correlated. Consuming fruits and vegetables regularly has been demonstrated to lower the chance of developing cardiovascular illnesses and cancer, making them vital food groups for a healthy lifestyle. In addition to minerals and vitamins, fruits and vegetables also contain phytochemicals that appear to enhance their nutritional worth. It is possible that fruits and vegetables' phytochemical composition, rather than their vitamin (vitamin A, vitamin C, and β-carotene) concentration, is what protects them from cancer and other chronic illnesses. Furthermore, it is believed that phytochemicals in the same meals have an even stronger antioxidant effect than these vitamins do. Thiols are a particular class of mercaptan distinguished by the presence of a sulfhydryl functional group. Biologically generated thiols, also known as biothiols, are the primary antioxidants that shield cells from oxidative damage of any type.Glutathione, also known as L-glutamyl-L-cysteinyl-glycine or GSH, is a well-researched biothiol that functions as an antioxidant to shield cells from oxidative stress. Glutathione synthetase converts γ-glutamyl cysteine (GGC) into it. In addition, GSH contributes to the reductive mechanisms necessary for DNA and protein synthesis. Besides storing and transporting cysteine (CYS), it also plays a co-enzymatic role in a number of processes involving external substances. Normal cells have been shielded against radiation and anticancer drugs using CYS and GSH delivery molecules. The metabolism of the necessary amino acid methionine produces the thiol amino acid homocysteine (HCYS). Recent research suggests that HCYS contributes to the pathophysiology of atherosclerosis by inducing damage through oxidative stress. N-acetylcysteine (NAC), another thiol molecule, functions as an antioxidant and a precursor to GSH. NAC is the preferred medication for paracetamol intoxication and has long been used as a mucolytic agent to treat chronic bronchitis. It is also a potent antidote for paracetamol toxicity. Because of its terminal sulfhydryl group, the synthetic thiol captopril, which inhibits the angiotensin converting enzyme (ACE),

has also been suggested as a free radical scavenger.

1.5.1 Biologically Important Thiols in Various Vegetables:

Table 1 listed the amounts of NAC, CAP, GSH, GGC, CYS, and HCYS in different vegetables. Among biological thiols, asparagus possesses the highest concentrations of GSH and NAC, measuring 349 and 46 nM/g wet weight, respectively. With 349 nM/wet weight, red pepper has the highest level of CYS. Only red pepper and asparagus have HCYS, while only spinach and green beans contain GGC. At 11 nM/g wet weight, the amount of HCYS was found to be much higher than that of red pepper. At 23 nM/g wet weight, the amount of GGC was found to be higher than that of green beans. The veggies with the lowest thiol levels that were found are listed below: Tomatoes had the lowest NAC level (3 nM/g wet weight), broccoli and carrots had the lowest GSH level (4 nM/g wet weight), avocados had the lowest CYS level (4 nM/g wet weight), red peppers had the lowest HCYS level (5 nM/g wet weight), and spinach had the lowest GGC level (4 nM/g wet weight). Moreover, no biological thiols were detected in cabbages, and the only food item that included CAP was asparagus (28 nM/g wet weight).

Vegetables	mean ± SD (n = 3)				
	NAC	GSH	CYS	HCYS	GGC
Asparagus	46 ± 1	349 ± 26	122 ±1	11±1	ND
Spinach	ND	313 ± 33	84 ±2	ND	4 ± 0
Broccoli	ND	4 ±1	ND	ND	ND
Cauliflower	ND	6 ±1	7±1	ND	ND
Green squash	ND	47 ± 11	6 ±1	ND	ND
Yellow squash	ND	39 ±8	27 ±6	ND	ND
Cucumber	6 ± 1	123 ± 38	11 ±3	ND	ND
Carrot	ND	4 ±0	ND	ND	ND
Parsley	9 ±1	17±9	8±1	ND	ND
Tomato	3 ±1	64± 10	55 ±3	ND	ND
Red pepper	25 ±4	42± 2	349 ± 18	5 ±1	ND
Green pepper	12 ±2	8±1	9±1	ND	ND
Potato	ND	5 ±0	ND	ND	ND
Avocado	ND	339 ± 10	4 ±1	ND	ND
Green beans	ND	230 ±2	67 ± 11	ND	23 ± 1

aND, not detectable. CAP was only detected in asparagus (28 ± 6 nM/g wet weight). The results are given as means standard deviations of three samples of each vegetable.

1.5.2 Biologically Important Thiols in Various Fruits:

Table 2 demonstrated the quantities of GSH, CYS, GAC, and NAC for various fruit kinds. Among the biological thiols, strawberries had the greatest concentrations of CYS and NAC, at 59 and 5 nM/g wet weight, respectively. In the papaya, the greatest level of GSH was measured at 136 nM/g wet weight. Only the papaya (42 nM/g wet weight) contained GGC. The only thiol (7 nM/g wet weight) identified in bananas was CYS. The lowest concentrations of GSH, CYS, and NAC among biological thiols are found in lemons (4, 5, and 6 nM/g wet weight, respectively). Moreover, no biological thiol was detected in apples, peaches, blackberries, or red grapes.

Fruits	mean ± SD (n =3)		
	NAC	GSH	CYS
Orange	ND	5 ± 11	41 ± 2
Lemon	4 ±0	5±0	6± 0
Grapefruit	4 ±0	13 ±3	15 ± 2
Mango	ND	59 ±6	10 ± 0
Papaya	ND	136 ± 12	58 ± 5
Banana	ND	ND	7 ± 0
Strawberry	5 ±1	39 ±8	59 ± 5

a ND, not detectable. GGC was only detected in papaya (42 ± 3 nM/g wet weight). The results are given as means ± standard deviations of three samples of each fruit.

Vegetables and fruits varied greatly. Asparagus, for instance, has the greatest GSH and NAC levels (Table 1). According to recent research, the GSH found in a variety of meals may improve the excretion or reduce the absorption of oxidised lipids, hence increasing their removal. Furthermore, it has been demonstrated that eating foods high in GSH can reduce the incidence of oral and pharyngeal cancer by 50%. The amount of thiols depends on a number of factors, including the region, environment, storage method, length of storage, and cooking technique. According to one study, processing a variety of foods, including grapefruit, tomatoes, spinach, carrots, apples, peaches, and sweet potatoes, considerably reduces the mean GSH content by 87%. Frozen strawberries and reconstituted frozen oranges, on the other hand, maintained high levels of GSH in the same trial. According to this study, GSH levels need to be closely examined, especially in processed diets. Since earlier research, the biological significance of the variations in thiol content discovered in each vegetable and fruit has not been examined. only highlight how GSH, NAC, and CAP affect different illnesses. In order to ascertain these thiols' biological effects, they were administered as pure compounds in these investigations. In order to ascertain the impacts, we plan to give animals some of the vegetables that, for instance, have the greatest GSH levels while keeping an eye on the results.

Thiyl Radical: A short discussion:

2.1 Introduction:

Nature has employed thiyl radicals in a wide variety of biological reactions. As exemplified by the crucial deoxygenation of ribonucleotides—a transformation that is shared by all living things in the de novo production of DNA precursors—thiol residues are involved in numerous enzymatic processes. These radicals are found in biological systems almost everywhere due to a variety of features, such as their remarkable reactivity and ease of production from a variety of sources. It is not unexpected that synthetic chemists are also interested in these radicals, as they are central to certain incredibly effective radical reactions. It is well known that thiyl radicals effectively add to a variety of unsaturated systems, including thiocarbonyl groups, alkenes, and alkynes. Most of these reactions are very versatile since they may be reversed, and the ß-fragmentation of 2-sulfanylalkyl radicals is a crucial step in the chain propagation of many transformations. Reactions involving extremely selective abstraction of hydrogen atoms demonstrate how special thiyl radicals are for designing complex reactions without the need for metal catalysis. In the 1990s and over 40 years ago, the chemistry of thiyl radicals was reviewed. Certain facets of this chemistry, including radical cyclizations, the thiol-ene coupling reaction, and the thiol-yne reaction, have been compiled more recently.

2.2.2 Kinetic and thermodynamic aspects of reactions involving thiyl radicals:

Kinetic research on tiny organic radicals have always come before the development

of synthetic techniques, as a thorough understanding of the characteristics of a reactive species is essential to planning synthetic reactions. The primary basic reactions involving thiyl radicals are described in the section that follows, along with a discussion of the variables influencing the rates and selectivity of these reactions. The gas-phase chemistry of thiyl radicals will not be described as it is outside the purview of this Review; only investigations conducted in the liquid phase have been taken into account. The information provided here may be pertinent to the function of thiyl radicals in biological systems, even if the primary focus of this Review is synthetic reactions.

2.3 Generalities:

3.1 S−H Bond Dissociation Energies in Thiols:

Due to their comparable S-H bond dissociation energies, which are usually estimated to be around 87 kcal mol−1, alkane thiols behave practically all similarly towards hydrogen atom abstraction, regardless of the structure of the alkyl residue. Cysteine's S-H bond is marginally weaker (86 kcal mol−1) compared to hydrogen sulphide, which has a much lower reactivity (91 kcal mol−1). The homolytic reactivity of thioacids is generally similar to that of alkanethiols, with the S-H bond falling within the same range (87 kcal mol−1 for thiobenzoic acid to 88 kcal mol−1 for thioacetic acid). Because the associated arenethiyl radical is stabilised by resonance, thiophenols are good donors of hydrogen atoms. The S-H BDE of thiophenol is approximately 79 kcal mol−1, although substituents on the ring can significantly affect this value [49]. Regarding the X-H bond in phenols (X = O) and anilines (X = N), para-substituents that donate electrons reduce the S-H BDE while those that withdraw electrons enhance it. According to computational research, the primary cause of the BDE difference is the (de)stabilization of the arenethiyl radical; substitution has very little impact on the parent molecule's energy. Therefore, in comparison to pentafluorothiophenol (estimated at 84 kcal mol-1) [53] and paranitrothiophenol (82 kcal mol−1), the S−H bond of 4-aminothiophenol is notably weak (70 kcal mol−1). The strength of the S-H bond is largely unaffected by certain substituents, such as halogen atoms and the trifluoromethyl group, despite significant fluctuations in pKa and redox potentials. Although hydropersulfides (RSSH) contain very weak S-H bonds (about 65 kcal mol−1), they are hardly employed in synthetic procedures.

3.2 The S−S Bond Dissociation Energies in Disulfides:

In disulfides, the sulfur-sulfur bonds exhibit greater strength compared to the isostructural O−O, Se−Se, or Te−Te links. Disulfides are effective thiyl radical precursors, particularly helpful when a nonreductive environment is needed, because the S-S can be readily cleaved. The S−S BDE, which is approximately 65 kcal mol−1 for dialkyldisulfides and 50 kcal mol−1 for diaryldisulfides, is determined by the stability of the resultant radical.

3.3 Generation of Thiyl Radicals:

One of the main sources of thiyl radicals is the interaction between molecules containing sulphur and another radical. A hydrogen atom can be quickly transferred by thiols to the majority of radical X• types, which have greater X-H BDEs. In order to start thiol-mediated radical transformations, all of the frequently utilised initiators—such as azo-compounds or peroxides—that produce alkyl or alkoxyl radicals are effective. Organoboranes are good producers of alkyl radicals and can be employed with oxygen to start chain reactions at low temperatures. One can produce thiyl radicals by combining a thiol with an electron-rich oxidant, like Mn(III) compounds. Similar to this, it has been

claimed that the autoxidation of thiolate solutions involves the generation of thiyl radicals as a result of electron transfer from thiolate anions combined with oxygen. Some very effective radical chain activities that occur in the absence of radical initiator may be initiated by residual oxygen in solutions when the autoxidation of thiols continues through the production of thiyl radicals. Thiyl radicals, on the other hand, are produced when homolytic substitutions occur at a sulphur atom in disulfides. When it comes to diaryldisulfides, the reaction is more effective than when it comes to dialkyldisulfides (2 × 105 and 6 × 104 M−1 s−1 for a main alkyl radical at 298 K, respectively). Among other things, tin-centered radicals can also encourage this activity. A disulfide radical anion is created when electrons are transferred to disulfides; upon protonation, this anion splits into a thiyl radical and a thiol. It is possible to cause homolytic cleavage of S-H or S-S bonds through light irradiation or radiolysis. Different dissociation mechanisms may be involved in the absorption of thiols at low wavelengths (maximum of absorbance at 200 nm and a broad band centred at 235 nm for methanethiol). Therefore, it is not very effective to produce significant numbers of thiyl radicals by radiation over 300 nm. But even through Pyrex glass, continuous solar radiation can be employed for preparative chain reactions in which only initiation is needed (cutoff approximately 280 nm). Because the steady-state concentration of radicals remains low in these situations, the gradual but consistent initiation is advantageous and lessens the significance of termination reactions. Because the triplet state of carbonyl compounds quickly abstracts a hydrogen atom from thiols, ketones are frequently used as light-irradiation sensitizers. Diphenyldisulfide has been irradiated at 355 nm in flash photolysis experiments, and because the S-S bonds in disulfides are much weaker than any S-H bonds, they are easier to cleave photochemically. When nitrosyl chloride or a diazonium salt react with a thiol, respectively, thionitrites (RS−NO) or diazothioethers (RN=NSR′) are thermally decomposed and can produce thiyl radicals.

3.4 Detection of Thiyl Radicals:

The identification of thiyl radicals has been examined in other publications; for further references, the reader is referred to these works. Alkylthiyl radicals are often EPR quiet in solution, despite the possibility of solid state spectra. This is because to their extremely short spin−spin relaxation periods (T2), which significantly broaden the signal and lower the signal-to-noise ratio—often below the detection limit. For alkoxyl radicals, spin-orbit coupling between degraded orbitals in the radical's ground state is the cause of this phenomenon. EPR spectroscopy was able to observe the thiyl radicals that were created when a muon was added to a thiocarbonyl group because the subsequent symmetry change lifted the singly occupied orbital's degeneracy. Thiyl radicals have been identified as their nitroxyl radical adducts using nitrones] and nitroso spin-traps. However, only when the thiyl radicals are generated in situ can they be detected due to the limited stability of the radical adducts, since the nitroxyl radical quickly decays when initiation is interrupted. UV spectroscopy can be used to detect thiyl radicals, and laser flash photolysis has proven to be a useful technique for determining how reactive they are.27 Arenethiyl radicals are more easily detected than alkylthiyl radicals due to their larger UV-vis absorption band (about 500 nm); nevertheless, the latter have a weaker absorption band at approximately 330 nm.

5. Conclusions

The reactions of the cobalt-superoxo complex have been chosen to study in detail because

1. Superoxo radical species participates in the metabolic processes.

2. Reactions of superoxo species have dealt with disproportionations in systems featuring substitution–labile transition metal centres (transformations which are presumably related to the action of superoxide dismutase in bio-systems).

3. The compounds containing superoxo bridges are of particular interest as their redox behaviour in solution may elucidate the behaviour of biologically important molecular oxygen carriers.

4. Dioxygen activation chemistry by metal complexes is of great importance as they elaborate the reaction mechanisms of metalloproteins in biological systems.

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