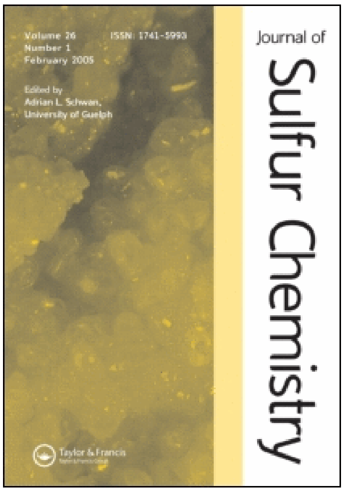

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Review Article

The chemistry of aqueous S(IV)-Fe-O_2 system: state of the art

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The aqueous Fe-S(IV)-O_2 system is kinetically superior to pure O_2 in oxidizing inorganic (e.g., As(III) to As(V), S(IV) to S(VI)) or organic (e.g., phenol) compounds and can achieve E_H levels (>1.3 V) that exceeds the O_2-H_2O couple. Fe-S(IV)-O_2 is important in various geochemical, biochemical, atmospheric, and industrial processes, and thus much effort has been devoted to understanding the mechanistic aspect of its redox chemistry. Despite the many advances made recently, Fe-S(IV)-O_2 redox chemistry has not been fully understood and elucidated. Clarification is needed on the redox chemistry of Fe-S(IV)-O_2: from a mechanistic level (e.g. mode of catalysis, effects of ligand) to its relative importance in various natural processes (e.g., acid rain formation). We attempt to initiate some of these clarifications by: 1) critically examining experimental results, conclusions, and disagreements found in literature, 2) considering the Fe-S(IV)-O_2 system in the light of other relevant chemistries, 3) highlighting difficulties in experimental practice that can interfere with the chemistry of Fe-S(IV)-O_2, and 4) discussing future research needs. This review ends with a large compilation of available thermodynamic properties (complex stability constants, E°_H) and kinetic data (rate expression, rate constants) relevant to Fe-S(IV)-O_2 system.

Keywords: Aqueous S(IV); Transition metal ions; Oxysulphur anions/radicals; Reaction mechanisms; Rate constants; Thermodynamics

1. Introduction

1.1 *Historical studies on Me^{n+}-S^{IV}-O_2 and its applications*

The Fe-S(IV)-O_2 system has been of great industrial and academic interests since the last century. In early 1900's, accelerated aqueous S(IV) oxidation by O_2 in the presence of trace transition metal ion, Me^{n+}, was observed [1]. Catalytic oxidation of alcohols [2] and transition metal ions [3] by Me^{n+}-S^{IV}-O_2 were also found. As early as the 1920's, an air-SO_2 mixture has been used for producing ferric sulphate and sulphuric acid from ferrous sulphate [4]. Other important industrial processes involving Fe-S(IV)-O_2 (or the generic Me^{n+}-S(IV)-O_2) include treatment of mining effluents containing cyanide [5, 6], extraction of valuable metals from metal concentrates/smelter slag [7–10], flue gas desulphurization [11–14], and destruction of organic pollutants [15]. SO_2-O_2 chemistry is also of great interest to food industry. S(IV) is

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important for wine making [16], fruit preservation [17], or as dehydrated food additive [18] and textural altering agents [19, 20]. More recently, the possibility of using SO_2-O_2 to oxidise As(III) to As(V) have also been investigated [21, 22]. After SO_2 was identified as one of the major contributors to acid rain, atmospheric chemists suggested Fe-catalyzed S(IV) oxidation may be a major acid rain production pathway [23–25]. Since then, much effort has been devoted to understanding the mechanism and kinetics of SO_2 oxidation in the atmosphere, where transitional metal ions, including Fe ions, are present at trace levels [26, 27]. Geochemists are also interested in the role Me^{n+}-S(IV)-O_2 plays in geochemical cycles and interactions such as the potential coupling [28] of marine reduced sulphurs [29] and air-borne metal dust [30] and redox chemistry involving reduced species and transition metals in acid mine streams [31, 32] or natural lake system [33]. Recently, biochemical investigation of the S(IV) metabolism [34] and toxicity [35] in human bodies, and its ability to damage DNA [36, 37] have also started. In all cases, the presence of iron (or some other transition metal ions) is the essential catalyst that accelerates oxidation of S(IV).

1.2 *Motivations of the review*

Many recent studies have looked into the complex mechanistic nature of the Fe-S(IV)-O_2 (or Me^{n+}-S(IV)-O_2) system in synthetic solutions [38–40] or environmental samples [6, 31, 41, 42]. They have employed various experimental techniques to test mechanistic hypotheses regarding different aspects of the system (e.g., predominant metal complexes [43, 44] and their relative catalytic importance [45], early time complexation and transformation dynamics [46, 47], inhibitory effects by organic species [48, 49], catalytic synergism [50, 51]), to probe the kinetics of particular reaction steps (e.g., radical-metal complex formation rate [52], intra-complex electron transfer rate [53], rate constants for elementary reactions involving oxysulphur radicals [54–56]), or to obtain thermodynamic properties of relevant species [57, 58]. Since the 1980's, reviews have tried to compile and condense the massive amount of data, hypotheses, models in literature and to elucidate the complex nature of Me^{n+}-S(IV)-O_2 systems [26, 27, 59–66].

Although many explorations and explanations have been made regarding the Fe-S(IV)-O_2 system, much of its chemistry still remained unclear. Because many studies were conducted in simplified, synthetic settings, the behavioural sensitivity of Fe-S(IV)-O_2 towards the synergistic stress (i.e., due to uncharacterized organic/inorganic species, mineral precipitations, system parameter fluctuations such as T, pH, ionic strength, irradiation, etc) is poorly characterized and understood. This difficulty, together with the intrinsic complexity of the system, has driven some studies to adopt a pragmatic approach by establishing rate expressions with key system parameter dependencies that are empirically determined [67]. As a result, the relative importance of Fe-S(IV)-O_2 in a real context (e.g. atmospheric waters, surficial aquatic systems, engineered systems) still needs to be determined.

For example, the O_3-S(IV) redox pathway, which is significant at alkaline conditions, only accounts for $\sim$10–30% of the sulphate production in marine boundary layer aerosols [68]. The relative contributions by H_2O_2, $^\bullet OH$, or Fe^{III} (and Me^{n+}) catalytic pathways are still unclear. In two other cloud/rain chemistry simulation studies [69, 70] where gas-water partitioning, physical transport, and extensive reaction networks (both aqueous and gaseous phase reactions) were considered, the role of Fe-catalyzed S(IV) oxidation remained ambiguous. The first study [69] reported $S(IV)_{(aq)}$ being converted to $S(VI)_{(aq)}$ at a rate of 3.7×10^{-9} $mol^{-1}s^{-1}$ for a typical urban cloud/rainwater composition. Modeling results showed that about 8% of S(VI) were formed via H_2O_2 (6%) or O_3 (2%) pathway while the rest are oxidised primarily by $Br_2^{\bullet-}$ (12%), $Cl_2^{\bullet-}$ (17%), and $^\bullet OH$ (64%) radicals. It is well known that oxysulphur radicals

($SO_X^{\bullet -}$, X = 2–5) and $^{\bullet}$OH can undergo interchange reaction with each other, and that $Br_2^{\bullet -}$, $Cl_2^{\bullet -}$, and $^{\bullet}$OH may all react with $S(IV)_{(aq)}$ (see C1 and C2 in Appendix C). Considering the huge network of radical reactions, it is thus very difficult to know how much of S(VI) formed is initiated by transition metal catalysis. The data presented in the second modeling study [70], however, indicated that atmospheric $S(IV)_{(aq)}$ was oxidised primarily by peroxo-species (H_2O_2 and HNO_4) depending on time of the day and their relative abundance. Likewise, the role of purely metal catalyzed S(IV) oxidation in colloidal suspension remains ambiguous when photo-induced oxidation also takes place [71].

It is generally accepted that the oxidation of Fe(II) to Fe(III) and the oxidation of S(IV) to S(VI) proceed much faster in an Fe-S(IV)-O$_2$ environment than in pure O$_2$. However, there have been disagreements on both the kinetic and the mechanistic aspects of these reactions [43, 44, 64, 67, 72–75]. Although studies over the last ten years have greatly favoured the radical chain mechanism in explaining the redox behaviour in aqueous Fe-S(IV)-O$_2$ system [48, 54, 60, 66, 76]; refs within [26, 65], wide discrepancies on rate constants for specific reactions [54] (see also rate constant variability in C1, C2, C5 in Appendix C), disagreement on interpretation of the chain mechanism network, and contradictory observations are still found in literature. Furthermore, alternative mechanisms have not been conclusively invalidated. Many studies have quoted the radical chain mechanism, but very few have provided experimental evidence for its functioning in the particular case (e.g., [36, 37]). In other cases where the metal catalyst is bound by a relatively large ligands, alternative mechanisms may indeed prevail [77]. Lastly, experimental results from many investigations were ‘problematic’ due to interpretational bias or analytical negligence. All these disagreements, discrepancies, and deficiencies prompt for clarifications

This review attempts to initiate some of these clarifications by: 1) critically examining experimental results, conclusions, and disagreement found in literature, 2) considering the Fe-S(IV)-O$_2$ system in the light of other relevant chemistries, 3) highlighting difficulties in experimental practice that can interfere with the chemistry of Fe-S(IV)-O$_2$, and 4) discussing future research needs. This review will end with compilations of available thermodynamic properties and kinetic data relevant to the chemistry of aqueous Fe-S(IV)-O$_2$ system.

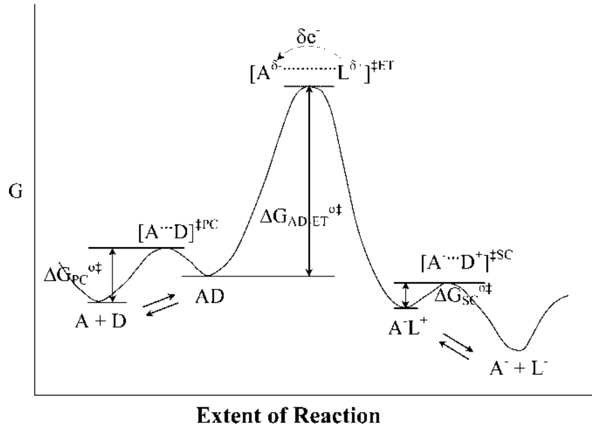
2. Overview on general redox chemistry [78–81]

2.1 *Thermodynamics of redox reaction*

The general thermodynamic relationships for redox reaction are very well established. The spontaneity of a proposed redox reaction depends on the free energy for the reaction, ΔG_{ET}, which can be related to the redox potential for the reaction ΔE_H. A redox reaction with $\Delta G_{ET} < 0$ will proceed spontaneously, but the rate of reaction is determined by the height of the activation energy barrier (see section 2.2). At thermodynamic equilibrium, $\Delta G_{ET} = 0$, and all redox couples present in the system should share the same pε or E_H.

2.2 *Kinetics of redox reaction*

2.2.1 Dependence of rate on activation energy. Redox reactions often have very favourable ΔG_{ET} but they proceed rather slowly [79, 81]. Scheme 1 illustrates how oxidant (e$^-$ acceptor, ‘A’) and reductant (e$^-$ donor, ‘D’) get transformed to A^- and D^+ through various energy states. The reactants first form a precursor-complex (PC) AD. A fraction of AD are energetic enough to overcome $\Delta G_{ET}^{o\ddagger}$, the free energy of activation for the electron transfer, and



SCHEME 1 Generic energy diagram for electron transfer reaction.

form the highly unstable transition complex $[A^{\delta-}\cdots L^{\delta+}]^{\ddagger ET}$. Completion of electron transfer results in the formation successor complex (SC), A^-D^+, which dissociates to give the final products, A^- and D^+. Assuming $\Delta G^{o\ddagger}_{ET}$ is much larger than $\Delta G^{o\ddagger}_{PC}$ or $\Delta G^{o\ddagger}_{SC}$, the overall rate, r_{ET}, is then proportional to the concentration of the transition complex. Arrhenius equation and transition state theory allow r_{ET} and $\Delta G^{o\ddagger}_{ET}$ to be mathematically related as [80]:

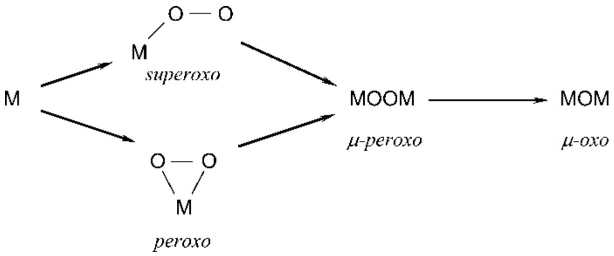
$$r_{ET} = \left(\frac{kT}{h}\right)\exp\left(\frac{-\Delta G^{o\ddagger}_{rxn}}{RT}\right)\{A\}\{D\} \approx \left(\frac{kT}{h}\right)\Delta G^{o\ddagger}_{ET}\{A\}\{D\} \tag{1}$$

The Marcus theory [78, 82] elaborates the meaning of $\Delta G^{o\ddagger}_{rxn}$ for electron transfer reactions in more concrete terms. It is shown that the free energy of activation for electron transfer is determined by the standard free energy of the reaction ΔG^{o}_{rxn} and the reorganization energy λ, which describes the energetic cost for electron to tunnel from optimal energy state of the e^- donor (i.e. bottom of 'energy well' of D) to that of the e^- acceptor (i.e. bottom of 'energy well' of A). Mathematically, $\Delta G^{o\ddagger}_{rxn}$ is expressed as:

$$\Delta G^{o\ddagger}_{rxn} = \frac{(\Delta G^{o}_{rxn} + \lambda)^2}{(4\lambda)} \tag{2}$$

2.2.2 Kinetics of oxidation by molecular oxygen [80]. Dissolved oxygen is known to exist predominantly as the ground state triplet oxygen (or dioxygen) $^3O_2$. The much more reactive singlet form, $^1O_2$, is much less abundant ($\sim 10^{-14}$ to 10^{-12} M $^1O_2$ in natural waters [80]). Oxidation by triplet oxygen (or dioxygen) is often slow because reducing it to $O_2^{\bullet-}$ is thermodynamically unfavourable ($E^o_H(^3O_2/O_2^{\bullet-}) = -0.16\,V$), while reduction of singlet oxygen is quite favourable ($E^o_H(^1O_2/O_2^{\bullet-}) = 0.83\,V$) (see B8 in Appendix B). $^1O_2$ and other reactive oxidative species (ROS) (e.g., H_2O_2, $^\bullet OH$, $HO_2^\bullet/O_2^{\bullet-}$) [83] mediate stepwise reduction of $^3O_2$ [84], and thus the abundance of ROS essentially determines the overall rate of oxidation by molecular oxygen. In natural waters, ROS are primarily produced from the photolytic reactions of organic chromophores (e.g., dissolved organic matter DOM), hence their abundance is controlled by the intensity and duration of irradiation, the concentration of DOM, and the presence of oxidizable matters that serve as sinks for ROS.

2.2.3 Enhanced reactivity of molecular oxygen by transition metal ions. The presence of transition metal ions can improve redox reactivity of molecular oxygen (activation of



SCHEME 2 Structures of metal oxygen complexes.

oxygen) [85, 86] by forming metal-oxygen complexes such as a superoxo, peroxo and oxo structures (scheme 2) [87]. Dioxygen can also form an adduct with transition metal ions complexed by polydentates (i.e. Me^{n+}-L_{poly}) via a superoxo configuration, with the unpaired electron resonated in the dioxygen structure [88–90]. Due to the stronger electron affinity of O than metal ions, electron density on the metal center is partially drawn/transferred to $-O_2$ (i.e. L"-$Me^{(n+\delta)}$-$^{\delta-}O_2^{\bullet}$), with the extent of transfer dependent on the nature of the polydentatic ligand as well as its substituent functionalities [90]. Well known examples of Fe-L_{poly} capable of forming adduct with $^3O_2$ are hemoglobin [88] and cytochrome [89], which are essentially Fe complexed by porphyrins. Both are actively involved in biochemical electron transfer reactions – the former as oxygen carrier, the latter as oxygenase [89, 91]. Qualitatively, the catalytic promotion of dioxygen redox activity in the presence of transition metal ions can be understood as a lowering in activation energy to the transition state (or $E^\circ_H(\text{Me-}O_2/O_2^{\bullet -}) > E^\circ_H(^3O_2/O_2^{\bullet -})$).

3. Speciations in aqueous Fe-S(IV)-O$_2$ system

3.1 *Dissolution of $SO_{2(g)}$ and speciation of aqueous S(IV) oxides*

$SO_{2(g)}$ is very soluble in water when compared to $O_{2(g)}$ and other gases (see Appendix A). Dissolved S(IV) oxides exist mostly in three major forms, $SO_2 \cdot H_2O$, HSO_3^- and SO_3^{2-}. Reactivity of aqueous S(IV) depends strongly on its speciation. Previous studies have suggested that SO_3^{2-} is about 20–40 times more reactive than HSO_3^-, which in turn is about 50 times more reactive than $SO_2 \cdot H_2O$ [92–94]. The equilibrium distribution of dissolved S(IV) can be estimated according to the following equation:

$$[\mathrm{S(IV)}] = [SO_2 \cdot H_2O](1 + K_{a1}\{H+\}^{-1} + K_{a1}K_{a2}\{H+\}^{-2}) \tag{3}$$

Where K_{a1} and K_{a2} are the acid dissociation constants for $SO_2 \cdot H_2O$ and HSO_3^-, respectively. Acid dissociation constants for selected acids are tabulated in B1 and B2 in Appendix B. If the solution is in equilibrium with $SO_{2(g)}$, $[SO_2 \cdot H_2O]$ is related to the partial pressure of $SO_{2(g)}$, P_{SO2}, by Henry's Law constant (Appendix A).

Aqueous HSO_3^- has two tautomeric forms: bisulphite ion (form I, $HOSO_2^-$) and sulphnate ion (form II, HSO_3^-) (see D.1 in Appendix D for structural configurations). More evidence is pointing towards bisulphite ion as the dominant species [26]. Furthermore, tautomeric form II can best explain the reactivity of HSO_3^- [63]. However, a recent *ab initio* study showed that the sulphnate ion is more stable in both gaseous phase and aqueous phase by about 32–40 kJ mol^{-1} [95]. In this review, HSO_3^- will mean a sum of both tautomeric forms. At high HSO_3^- concentration, dimerization can occur to produce disulphite ion, $S_2O_5^{2-}$ ($K_{dimer} = 7 \times 10^{-2}\,M^{-1}$ [55]) [26, 96, 97]. However, disulphite is a minor form of S(IV) and accounts for no more than 3% of total S(IV) [26] and so it may be practically neglected [98].

3.2 *Speciation of aqueous Fe ions*

3.2.1 Monomeric speciation of Fe in water. Transitional metal ions, including Fe(II) and Fe(III) ions, do not freely exist in water. They are always coordinated with ligands. In the absence of other ligands, they are coordinated with H_2O, the most abundant ligand in aqueous system. In the 'free' state, both Fe^{2+} and Fe^{3+} are complexed by six water molecules (i.e. $Fe(H2O)_6^{2+}$ and $Fe(H2O)_6^{3+}$). The coordinated water molecules will be left out, and the aqua-complexes abbreviated as Fe^{2+} or Fe^{3+} hereafter.

Fe ions also hydrolyze water to form Fe-hydroxo complexes, i.e.:

$$Fe^{2+/3+} + H_2O \longrightarrow FeOH^{+/2+} + H^+ \tag{4}$$

Thus addition of Fe(II) and Fe(III) increases system acidity [26]. The dominant Fe(II) form in water up to pH 7 is $Fe(H_2O)_6^{2+}$ [99]. Speciation of Fe(III) in water, however, is more complicated as it can exist in several hydroxo forms, each of which dominates over different pH ranges. At elevated pH, the total Fe(III) concentration is constrained by precipitation. A list of Fe(II)- and Fe(III)-hydroxo complexes and their formation constants can be found in B3 and B5 in Appendix B.

3.2.2 Hydrolytic polymerization of Fe(III) in water. Fe(III) speciation is further complicated by the issue of hydrolytic polymerization at low pH [100]. Polymerization of Fe(III)-hydroxo complexes starts with dimerization and formation of small, multi-meric complexes (2–4 nm spherical structures; $t \sim 10^2$–10^3 s). These complexes will be converted into red cationic polymer. These polymers will go through a relatively slow aging phase, in which they are gradually converted to oxide phases through the removal of H from the entity ($t \sim 10^6$ s). Upon maturity, polymeric oxide phase will precipitate out of the aqueous phase ($t \sim 10^8$ s) [101–104], the speed of which depends on the nature and valencies of anions. Depending on the stage and time of aging, these polymer may range from 10^3 to 10^4 units [102, 105].

The polymerization mechanism essentially involves the bridging of Fe centers via oxygen species (OH^-, O_2^-) and the release of H^+ with more monomer addition. Thus, as Fe(III)-hydroxo polymers age, the OH^-/Fe ratio increases (OH^-/Fe ratio: ~1 to 2 for fresh polymers; ~2.5 for aging time <1 d; ~2.8 for >10 d) and the system pH decreases. An ultimate lowest pH is expected as the polymerization reaches a limit [104, 105].

Hydrolytic polymerization is sensitive to pH, presence of other anion species, and Fe(III) concentrations. Addition of a small quantity of base to an Fe(III) solution containing NO_3^-, Cl^-, or SO_3^{2-} can trigger rapid formation of hydrolytic polymer. Also, the formation of such precursor complex for $Fe_2(SO_4)_3$ is kinetically favoured at lower pH to the formation of Fe(III)-monovalent anionic complexes.

3.2.3 Lability and reactivity of Fe-hydroxo complexes. In general, Fe(III) becomes more reactive when it is coordinated with OH^-. For instance, $FeOH^{2+}$ is about a few hundreds times more reactive than Fe^{3+} [46, 107]. This has been attributed to the translabilization effect of the OH^- ligand [26]. Furthermore, coordinated water molecules are more labile in the monohydroxo complex than in the hexaaqua complex [46, 108], probably due to the stabilization effect of OH^- on the Fe center. It is important to note, however, that metal ions in complexes with dimeric, trimeric, and multi-meric nuclei tend to react slower than those in monomeric complexes [100].

3.3 *General consideration on the stability and speciation of Fe-S complexes*

3.3.1 Relative coordination strength of ligand. The magnitude of the complex formation constant [79, 81], β, (most simplified case, $\beta = \{Me^{n+}L^{w-}\}\{Me^{n+}\}^{-1}\{L^{w-}\}^{-1}$), for a complex is reflective of the strength of the metal-ligand(s) interaction. A high value for β implies the coordinated state is thermodynamically much preferred to the dissociated state, and thus the resulting complex is more stable. An example of this is Fe-EDTA complexes. Conversely, a low value for β would mean that the binding ligand is rather labile – it is equally 'comfortable' (or 'uncomfortable') in the dissociated or the coordinated form. An example of this is $Fe^{II/III}$-Cl_X complexes (logβ roughly from 0.4 to 2).

The ability of a ligand to form a stable complex with a metal ion may not be inferred from its order in the spectrochemical series. For instance, in the series, H_2O is known to have a higher order than oxalate ($C_2O_4^{2-}$), with OH^- as the 'weakest' ligand of the three [109, 110]. Yet, $Fe^{III}OH^{2+}$ ($\log\beta \sim 12$) is about three orders of magnitude more stable than $Fe^{III}C_2O_4^+$ ($\log\beta \sim 9$) (see B6 in Appendix B), and OH^- exerts a greater stabilization effect than H_2O on metal center (see section 3.2.3).

Although different mechanistic models have been offered to explain the catalytic redox activity in Fe-S(IV)-O_2 system, the critical role of Fe-S(IV) complexes being the rate determining species is unanimously recognized [26, 27, 59–66]. Thus it is important to understand how Fe-S complexes may be affected by the presence of other ligands.

3.3.2 Relative stability of Fe-sulphato^{VI} vs Fe-sulphito^{IV} complexes. Sulphite or related species can complex with metal ions in different ways. They can be bonded to the metal center through one single atom (S or O) or two atoms (S and O, or O and O). The O-bonded sulphito complexes could further undergo substitution, linkage isomerization and electron transfer reactions [43]. It has also been claimed that a more willing electron donating bonding-atom would form a more stable complex with the metal ion [44, 72]. Since S is less electronegative than O, it was expected that an S-bonded complex would be more stable than an O-bonded metal-sulphito complex. Another study [111] claimed that whether the metal-sulphito complex is S-bonded or O-bonded depended on the inertness of the metal complexes: an inert metal complex would form a S-bond with a sulphito group, whereas a labile complex would have a O-bond. Kraft and van Eldik [43, 73], however, stated that the O-bonded sulphito complexes were typically formed by nonlabile octahedral metal hydroxo species whereas the labile species would form S-bonded complexes. Various atmospheric groups have also suggested that pH has a critical role in controlling the structure of metal complexes and their relative distribution [112, 113].

Fe-sulphato complexes are generally much less stable than Fe-sulphito complexes. For instance, $\log\beta(Fe^{II}SO_3) \approx 8$–$9) > \log\beta(Fe^{II}SO_4) \approx 2$; $\log\beta(Fe^{III}SO_3^+) \approx 7 > \log\beta$ $(Fe^{III}SO_4^+) \approx 3$; $\log\beta(Fe^{III}(SO_3)_2^-) \approx 18) > \log\beta(Fe^{III}(SO_4)_2^-) \approx 5.5$ (see B3 and B5 in Appendix B). If one may assume that the oxygen atoms bonded to the sulphito-S and the sulphato-S have more or less the same electron density around themselves, then the relative difference in Fe-sulphito and Fe-sulphato complexes must be rooted in the difference between sulphito-S and sulphato-S. Sulphato-S^{VI}, being more deprived of electron density when compared to sulphito-S^{IV}, should be less willing to associate with the electron-deprived Fe ion. Thus it may be argued that both sulphate and sulphite are bound to $Fe^{II/III}$ via a Fe-S linkage (rather than Fe-O) in a substantial fraction of Fe-$S^{IV/VI}$ complexes. Thus, it seems unlikely for Fe and sulphite/sulphate to interact through an O-Fe-O linkage, although Fe-S and O-Fe-S linkages still remain possible.

3.3.3 Effects of H^+ on the stability of Fe-S complexes. H^+ and OH^- are important species that will influence speciation chemistry of Fe-S complexes. By chemical intuition, association of $Fe^{II/III}$ and a protonated ligand (H^+L^{w-}) should be less favourable than the unprotonated ligand (L^{w-}). Rearranging the complex formation equation to the form of equation (5) with the corresponding equilibrium constant β' (equation (6)). The relative stability of the two forms can be compared by considering logβ', which can be derived from constants listed in B3–B6 in Appendix B.

$$Fe^{II/III} + H^+L^{w-} \longrightarrow Fe^{II/III}H^+L^{w-} \tag{5}$$

$$\beta' = \left\{Fe^{II/III}H^+L^{w-}\right\}\left\{Fe^{II/III}\right\}^{-1}\left\{H^+L^{w-}\right\}^{-1} \tag{6}$$

It can be shown that unprotonated ligands can indeed form more stable complexes with Fe ions ($\log\beta'(Fe^{III}SO_3^+) \cong 7 > \log\beta'(Fe^{III}HSO_3^{2+}) \cong 2$; $\log\beta'(Fe^{II}CO_3) \cong 5.5 > \log\beta'(Fe^{II}HCO_3^+) \cong 1.5$).

The effect of OH^-L^{w-} on complex stability is more ambiguous. Inconsistent trends are observed when comparing the formation constants between Fe-HL and Fe-OHL. It seems that in the presence of Fe(II), HL or OHL complexes are roughly equal in stability ($\log\beta$ about the same for $Fe^{II}HCO_3^+$ vs $Fe^{II}(OH)(CO_3)^-$, and for $Fe^{II}HEDTA^-$ vs $Fe^{II}OHEDTA^{3-}$). However, for Fe(III) complexes, OH^- does impose a pronounced stabilization effect ($\log\beta(Fe^{III}OH(SO_3)) \cong 19 > \log\beta(Fe^{III}HSO_3^{2+}) \cong 9$; $\log\beta(Fe^{III}OHEDTA^{2-}) \cong 34 > \log\beta(Fe^{III}HEDTA) \cong 29$).

3.4 *Formation and dissociation kinetics of Fe-sulphito complexes*

The forward and reverse rate constants for the formation/dissociation reactions of some Fe(II/III) complexes are listed in C8 in Appendix C. The intrinsic rates for other equilibrium reactions such as dissociation/formation of H_2O or HSO_3^- are also listed as references.

4. Reactions in aqueous Fe-S(IV)-O_2 system

In strict terms, Fe-S(IV)-O_2 is not a catalytic system because all three species are chemically transformed. The 'catalytic' nature of the system refers to its capability to accelerate, under appropriate chemical conditions, the oxidation rate by O_2. This rate enhancement feature is caused by the co-participation of the oxidative Fe(III) and reductive S(IV) in a series of redox reactions. The ultimate electron acceptor in the system is O_2, though other species such as Fe(III) may also be reduced. Energetically, the Fe(III)-S(IV) interaction in the presence of O_2 leads to a lower activation barrier for electron transfer reactions. The oxidation speed of molecular oxygen is greatly reduced when either Fe(III) or S(IV) is absent. For instance, Fe(II) exposed to molecular oxygen at pH 4 has a half-life of almost a year [81], while S(IV) exposed to pure oxygen is fairly stable until transition metals are added [114].

The overall redox behaviour of the system depends highly upon the relative dominance of the oxidative species (i.e. O_2, Fe(III)) versus that of the reductive ones (i.e. Fe(II), S(IV)). In natural or engineered systems, the presence of other oxidative and reductive chemicals will also influence the redox behaviour of Fe-S(IV)-O_2. Qualitatively, oxidation of Fe(II), S(IV), or other reductants will occur when the oxidative species are controlling. Under reducing condition, or insufficient O_2 supply, S(IV) oxidation will stop and Fe(III) reduction may occur. The [Fe(III)]/[Fe(II)] ratio, the initial ratio $[Fe]_{Tot}/[S(IV)]$ [66], as well as % SO_2 relative to O_2 [4, 39, 115] have been reported to dictate the system between its 'oxidative' and 'reductive' modes.

4.1 *Oxidation of chemical species by Fe-S(IV)-O_2*

$SO_{2(g)}$-$O_{2(g)}$ becomes a powerful and efficient oxidant in the presence of transitional metal ions such as Fe, Mn, Cu, Ni and Co [50, 64, 116, 117]. The oxidation of oxidizing Ni(II) and cyanide has been reported [5]. In another study, the oxidation of As(III) to As(V) was found to be enhanced by a 2% $SO_{2(g)}$ in $O_{2(g)}$ mixture in the presence of Fe(III) at pH 0.5–2 [22]. Complete degradation of phenol to CO_2 has also been observed in Cu(II)-SO_3^{2-}-O_2 at industrial conditions (80–110 °C, $P_{O2} = 1.5$–4.5 atm) [15]. Similarly, accelerated Fe(II) oxidation [4, 39, 74, 115, 118] and S(IV) oxidation [67, 73, 74, 114, 119] were also reported in various batch or semi-batch Me^{n+}-S(IV)-O_2 systems.

Regardless of the transformation direction, S(IV) is often oxidised. Sulphates (HSO_4^-, SO_4^{2-}) are the major oxidation products, though production of other species such as dithionate (S(V), $S_2O_6^{2-}$) [39, 73] and disulphate (S(VI), $S_2O_7^{2-}$) have also been observed or reported [120, 121]. For instance, dithionate production was observable at 9% SO_2, and it could account for as high as 15% of the oxidised sulphur at 15% SO_2 [39]. Its stoichiometric production from S(IV) oxidation can be expressed as:

$$2SO_3^{2-} + \frac{1}{2}O_2 + H^+ \longrightarrow S_2O_6^{2-} + OH^- \tag{7}$$

The selectivity between sulphate and dithionate depends primarily on the relative availability of O_2 and [S(IV)]/[Fe(III)] ratio. Dithionate production is usually preferred at high [S(IV)]/[Fe(III)] [122, 123], or low O_2 availability (section 5.2.3). The oxidation of S(IV) to sulphate is favoured in the presence of Cu(II), Cr(III), [122–125], though not Co(II), Mn(II), and Ni(II) [124]. According to [124], formation of dithionate is influenced by the initial pH, but is independent of the initial O_2 concentration. Their data showed that dithionate formation was maximum at pH 2.5.

$S_2O_7^{2-}$ production was first documented via laser Raman spectroscopy by Chang *et al.* [120] in non-catalytic S(IV) oxidation under high oxygen partial pressure and acidic conditions. It was believed to be a redox intermediate with very short half-life (~50 s) that undergoes hydrolysis to give sulphate:

$$S_2O_7^{2-} + H_2O \longrightarrow 2H^+ + 2SO_4^{2-} \tag{8}$$

The production of $S_2O_7^{2-}$ was also reported in a later investigation, also on non-catalytic S(IV) oxidation by O_2 [121]. Disulphate has been suggested to be an important intermediate in S(IV) oxidation with metal oxides as 'catalysts' [126, 127], though it is infrequently reported or measured.

Disregarding $S_2O_6^{2-}$ and $S_2O_7^{2-}$ as minor products, the oxidation of Fe(II) and S(VI) to higher states can be stoichiometrically expressed as in equation (9).

$$2Fe^{2+} + SO_2 + O_2 \longrightarrow 2Fe^{3+} + SO_4^{2-} \tag{9}$$

The overall catalytic oxidation of S(IV) can be expressed as in equation (10) when O_2 is relatively abundant and equation (11) when it becomes limiting [128].

$$SO_2 + H_2O + \frac{1}{2}O_2 \longrightarrow SO_4^{2-} + 2H^+ \tag{10}$$

$$SO_2 + 2Fe^{3+} + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2Fe^{2+} \tag{11}$$

4.2 *Reduction of species by Fe-S(IV)-O_2*

Reduction of Fe(III) to Fe(II) by S(IV) occurs when [Fe(III)] and [O_2] are relatively low to [S(IV)]. S(IV) is transformed to sulphate or dithionate ($S_2O_6^{2-}$) [39, 73, 74, 122, 129–132], depending on how much S(IV) is in excess [39, 122, 129] and the relative supply of O_2 [73, 74]. Krause [74] reported insignificant Fe(III) reduction rates at $[S(IV)]/[O_2] \leq 60$, though the corresponding [Fe(III)]/[S(IV)] values were not reported.

5. Redox behaviour of pure Fe-S(IV)-O_2 system

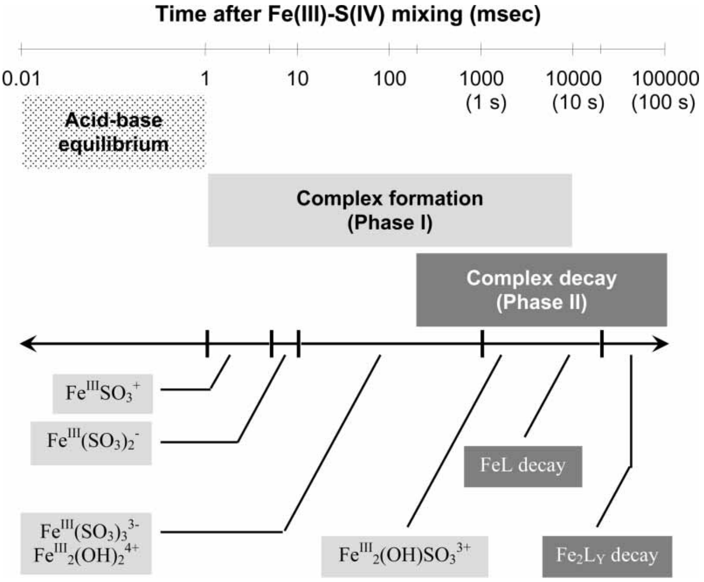
5.1 *Timeframe of transformation in aqueous Fe-S(IV)-O_2 system*

5.1.1 Timeframe for process kinetics. The overall transformation process can be divided into three periods: induction period, steady state or pseudo-steady state period, and completion period. Semi-batch and batch studies showed that, upon the co-presence of Fe(II/III), S(IV), and O_2, the system first goes through an induction period [4, 39, 74, 98, 133–135]. In industrial or engineered processes where S(IV)-O_2 and Fe(II) are continuously brought into contact and react, a true steady state will be established. In semi-batch (continuous supply of $SO_{2(g)}$-$O_{2(g)}$, fixed total [Fe]) mode, the induction period may be succeeded by a pseudo-steady state period [4, 39, 74] in which oxidation proceeds at fairly constant rates independent of the reductant level, most probably due to the limited supply of S(IV)-O_2 relative to reductant concentration. In the completion period, the oxidation rate declines as [Fe(II)] or [S(IV)] diminishes. The reaction timeframe in batch mode is more complicated. Steady O_2 consumption and H^+ production have been observed in batch mode [121]. However, the pseudo-steady state period may be absent if all reactants are equally limiting.

The length of the induction reflects the relative balance between the oxidative and the reductive species, and whether or not an optimal mixture of Fe-S(IV) and O_2 is present. For example, Tiwari *et al.* [4] found the duration of the induction period to be independent of initial [Fe^{3+}] but shortened as O_2 partial pressure increased; Zhang *et al.* [39] observed a shortened induction period with higher SO_2%.

5.1.2 Timeframe for species kinetics. Since Fe(III)-S(IV) interaction induces the rapid oxidation by O_2, the relative timeframe for the formation and decay of various Fe(III)-S(IV) complexes will shed light on the catalytic nature of the system.

A skeletal timeframe for identified Fe(III)-S(IV) complexes is shown in scheme 3. These complexes are formed in sub-second timescale. Chemical equilibrium between Fe(III)-S(IV) complexes and their constituent ions are essentially established within the first 200 ms after mixing (phase I in scheme 3) [43, 45, 73, 136, 137]. Formation of mono-nuclear-mono-ligand complexes are completed first, followed by that involving three constituents (e.g., Fe^{III}-bis(sulphito) complexes) or more [43, 45, 136]. This cascading pattern of simple complex formed first can be explained kinetically by the fact that all compounded complexes (e.g., $Fe_2^{III}(OH)_2^{4+}$) are built from the binding of simple complexes (e.g., $Fe^{III}OH^{2+}$) with another ligand or complex. Formation of $Fe^{III}SO_3^+$, $Fe^{III}(SO_3)_2^-$ (cis- and trans-), and $Fe^{III}(SO_3)_3^{3-}$ were reported at acidic, excess S(IV) conditions [43]. Analysis of absorbance spectra in early times showed that the bis(sulphito) complexes were formed within 5–10 ms, whereas the formation timeframe for tris(sulphito) complex was about 10–200 ms. The longer formation period for Fe(III)-tris(sulphito) complex can be understood by its dependence on excess S(IV). In a similar study at acidic but excess Fe(III) condition, $FeSO_3^+$ formation was



SCHEME 3 Timeframe for Fe(III)-S(IV) complexes formation and decay.

observed again within the first 200 ms [137]. Due to excess Fe(III), dimerized hydroxo complex ($Fe_2^{III}(OH)_2^{4+}$) formation was also observed [138]. The dimerization equilibrium between $Fe_2^{III}(OH)_2^{4+}$ and $FeOH^{2+}$ was coupled to the formation of $Fe_2^{III}(OH)SO_3^{3+}$, and the formation timeframe was identified to be from 1 to 10 s [45]. The more varied and later formation period for $Fe_2^{III}(OH)SO_3^{3+}$ can again be explained by the extended time needed to $Fe^{III}OH^{2+}$ and $Fe^{III}SO_3^+$ to meet and interact. Conklin *et al.* [136] observed roughly two kinetic phases. The first phase ($\tau_{1/2} \sim 3$ ms) was believed to correspond to formation of $FeSO_3^+$ from $FeOH^{2+}$ and S(IV), while the second phase ($\tau_{1/2} \sim 30$ ms at excess S(IV), $\tau_{1/2} \sim 200$ ms at excess Fe(III)) may be related to isomerization from Fe-SO_3 to Fe-OSO_2 linkage [136, 139]. The two-phase distinction was consistent with the findings in an earlier study [140].

The complex formation phase, which ends roughly at around 200 ms to 1 s, is succeeded by a decay phase for Fe(III)-S(IV) complexes [43, 45]. Kraft *et al.* [73] commented that the complexes were unstable after phase I, and the decay phase corresponded to the intra-complex electron transfer reaction that took place between Fe(III) and S(IV). Based on kinetic analysis of absorbance, the decay of $Fe^{III}SO_3^+$ took place from about 1 to 20 s [43, 73], and the decay after 20 s was attributed to the intra-complex electron transfer in the compounded complexes such as $Fe^{III}(SO_3)_2^-$. The decay of $FeSO_3^+$ was observed to be about 10 times faster than that of the bis or tris(sulphito) complexes. Likewise, Lente *et al.* also attributed the decline in absorbance after ~10 s to the Fe(III)-S(IV) induced oxidation by O_2 [45]. The timeframe for subsequent chemical transformations is less well characterized.

The period or phase durations presented in scheme 3 are not absolute. They vary with temperature and pH. For instance, the formation phase was shortened from 200 to 50 ms as temperature was raised from 10 °C to 25 °C [45], and from 200 ms to 20 ms when pH was lowered from 2 to 1 [136]. Finally, both Kraft *et al.* and Lente *et al.* consistently found that oxygen did not influence the formation rate of Fe(III)-S(IV) complexes [43, 45, 73]. As a final note, it should be emphasized that the early-time period ($0 \sim 100$ s) is not the same as the 'induction' period mentioned in 5.1.1. The later refers to the delayed on-set of Fe(III)-S(IV) interaction as a result of highly reducing initial condition (e.g., high [Fe(II)] or [S(IV)]).

5.2 *Factors influencing redox chemistry in Fe-S(IV)-O_2 system*

5.2.1 Fe. It is generally agreed that Fe(III) is the active 'catalyst' that brings about the oxidative power of S(IV)-O_2 and that Fe(II) is catalytically inactive [26, 134, 141]. The critical role of Fe(III) in oxidation reactions involving $SO_{2(g)}$-$O_{2(g)}$ was demonstrated [21]. Induced S(IV) oxidation was observed to proceed less efficiently [64] or even stop [98] when Fe(II) was the dominant iron species. The non-catalytic or even prohibitive nature of Fe(II) is further confirmed by the its effect on the induction period (section 5.1.1). The induction period is extended in the presence of Fe(II) [4, 39, 74, 98, 133] but much shortened when started with Fe(III) [135]. It has been suggested that the redox unreactive or even prohibitive nature of Fe(II) may be caused by its stable interaction with SO_4^{2-} (see 5.2.8) [64, 98, 142].

However, Fe(II) catalyzed S(IV) oxidations have been reported, though Fe(II) did not catalyze S(IV) oxidation as efficiently as Fe(III) [64, 116]. It is unclear whether the catalysis was carried out by Fe(II) or by trace levels of Fe(III) [60].

5.2.2 Sulphites S(IV). Semi-batch investigations on Fe(II) oxidation by $SO_{2(g)}$-$O_{2(g)}$ showed that an optimal SO_2 % range exists for Fe(II) oxidation. Fe(II) oxidation rate decreases below this optimal range while Fe(III) reduction takes place at SO_2 % levels above it due to excess SO_2 input. The optimal SO_2 % range is strongly pH and temperature dependent. Ferron *et al.* [115] studied the reaction at 80 °C and pH 3.5 and found that the optimal SO_2 % to be between 2 to 5%. Zhang *et al.* [39] found the optimal SO_2 % to be about 14% and 2% at 40 °C and 80 °C, respectively.

5.2.3 O_2. O_2 is the ultimate electron acceptor while Fe(III) and S(IV) together serves the 'catalytic' role of kinetically inducing and speeding up redox reactions (section 4). It also partly determines the critical switch of the system between its oxidative role (section 4.1) and its reductive one (section 4.2). The selectivity of S(IV) oxidation products is also influenced by O_2. Podkrajšek *et al.* [143] observed minor dithionate ($S_2O_6^{2-}$) production only in Fe(III)-S(IV)-N_2 system while only sulphate was found in the presence of O_2. The exclusive $S_2O_6^{2-}$ formation under anoxic condition was similarly observed in non-catalytic S(IV) oxidation studies [38, 71, 144]. However, the data in [73] convincingly demonstrated that $S_2O_6^{2-}$ production was enhanced in the presence of O_2 and higher [Fe(III)].

5.2.4 [Fe(III)]/[S(IV)], [Fe(III)]/[Fe(II)], [S(IV)]/[O_2] ratios. These ratios determine the redox behaviour of Fe-S(IV)-O_2 system. When the system is characterized by high [Fe(III)]/[S(IV)], high [Fe(III)]/[Fe(II)], and low [S(IV)]/[O_2], the system behaves overall as an oxidant. On the contrary, when these ratios point in the opposite direction, the system redox tendency will be predominantly reducing. In the later case, oxidation of reduced species will proceed very slowly, until sufficient number of catalytically active metal centers (e.g. Fe(III)) has been generated.

In theory, all three ratios are important in determining the redox inclination of the system. In practice, however, often only one of them is controlling. The reason for this is analogous to the case of a multiple-reactants reaction where usually only one of them is limiting, or that among a series of sequential reaction steps, only one step is rate limiting for the entire scheme.

For instance, Brandt *et al.* [114] observed that when all dissolved oxygen was consumed the redox recycling of Fe would come to a halt, implying that the [S(IV)]/[O_2] was controlling. In another case where Fe(II) oxidation by SO_2-O_2 was studied, Tiwari *et al.* [4] found the duration of the induction period to be independent of initial [Fe^{3+}] but shortened as O_2 partial pressure increased. Qualitatively, this means that [Fe(III)]/[Fe(II)] was quite low (highly reductive) when compared to [S(IV)]/[O_2], and that the reductive tendency of the system could be reversed by supplying more O_2.

On the contrary, Zhang *et al.* [39] reported a shortened induction period with higher SO_2 % up to a point, implying the system catalytic activity had not reached its maximum and that it could be further boosted with more S(IV) ‘catalyst’. Such observation raises an important point about S(IV). Being a reducing species, excess S(IV) can prevent the system acting as an oxidant; however, as part of the ‘catalyst’, S(IV) is also needed for rapid oxidation. Hence a critical balance exists between the reducing nature of S(IV) and its catalytic character, whereas for Fe(III) and O_2, the more they are present, the better is the system, kinetically, as an oxidant.

In a recent review, Yermakov and Purmal [66] have attempted to characterize the boundaries for [Fe(III)]/[Fe(II)], [Fe(III)]/[S(IV)], and how these two ratios were related in the light of a radical-based mechanism (see section 6.2). However, the [S(IV)]/[O_2] ratio itself, as well as its relation to the other two ratios, were left out of the analysis. [S(IV)]/[O_2] may be of no consequence to atmospheric systems because O_2 is much more abundant than S(IV) in rain-, cloud-, or fog-waters. But in industrial processes or engineered systems, [S(IV)]/[O_2] is very likely to be important, as various studies on the Fe-$SO_{2(g)}$-$O_{2(g)}$ system have shown [4, 74, 75, 115].

5.2.5 pH. Acidity influences the Fe-S(IV)-O_2 redox chemistry primarily by affecting the speciation of Fe ions and S(IV), which in turn controls the concentration of catalytically active Fe-S(IV) complexes such as $FeSO_3^+$ [45, 73], $Fe(OH)(SO_3H)^+$ [60]. These complexes are thought to be the rate limiting species in the induced oxidation of Fe(II), S(IV), or other compounds. pH also controls the total amount of dissolved Fe ions by constraining the catalytically active Fe(III). Fe(III) precipitates readily with increasing pH, and the precipitated or polymerized Fe(III) are less redox-reactive compared with dissolved Fe(III) (section 3.2.2). This may partially explain why the S(IV)-oxidation rate generally declines with increasing pH.

Electron transfer reactions also depend strongly upon pH. Generally, anions in deprotonated form undergo oxidation more readily because of the relatively richer electron densities. This effect has been well-documented for the oxidation of organic compounds [80]. Similarly, deprotonated sulphites lose electrons more willingly than the protonated forms. Such trends can be observed for the rate constants reported for various elementary reactions (see C1 and C2 in Appendix C).

It is rather difficult to summarize the overall influence of pH on Fe(III)-S(IV) induced oxidation because a change in pH often favours one aspect (e.g., S(IV) in more reactive form) of the reaction kinetics and disfavours another (e.g., less Fe(III)). Literature has been reported with a widely varied reaction order in [H^+] dependence at different pH ranges and [Fe], [S(IV)], and [O_2] settings [26].

Yermakov and Purmal [60, 66] attempted to explain the influence of pH on catalytic S(IV) auto-oxidation in a systematic way. They plotted S(IV) normalized oxidation rate data from five studies [50, 133, 145–147] against pH, and tried to show that the general bell-shape rate date corresponded to the normalized distribution of $Fe(OH)SO_3H^+$, which they believed to be the rate determining complex (section 6.2.1). Although the $Fe(OH)SO_3H^+$ curve was systematically biased toward the lower pH regime and fitted well only the data from two of the studies, the plot did illustrate two important points. The first is that S(IV) oxidation is determined primarily by the speciation of some rate determining Fe(III)-S(IV) complexes, which in turn depends heavily on the system pH. The second is to affirm the general bell shape of rate vs pH, with an optimal oxidation range from about pH 3 to 5. This is consistent with the division of rate into a ‘high’ pH ($pH > 5$) and a ‘low’ pH ($pH < 3$) regime, as proposed by Martin *et al.* [67]. As the system pH moves away from the optimal pH 3–5 range, the oxidation rate of Fe(II) (or other low valency metal ions) or S(IV) is expected to decline, as shown by the results in other Fe(II) oxidation [39, 115, 148–150] and S(IV) auto-oxidation studies [94, 151]. The importance of speciation on oxidation rate is reinforced by an observation of Huss *et al.* [150] who showed addition of HCl (0.005–0.2 M) could extend the induction period (section 5.1.1) considerably (0.5–40 hrs) in catalytic Fe(II) oxidation.

pH also influenced oxidation product selectivities. For instance, dithionate ($S_2O_6^{2-}$) formation is generally favoured at high acidity [152] and at low O_2 levels [38, 71, 124] due to the suppression of sulphate production [152].

5.2.6 Temperature. The rate of Fe(II) oxidation catalyzed by S(IV) generally increases with temperature until an optimum point and declines with further temperature increase. Schlitt *et al.* [128] observed S(IV) oxidation rate increased with higher temperature up to a limit beyond which no further increase was found. Tiwari *et al.* [4] studied the Fe-$SO_{2(g)}$-$O_{2(g)}$ system from 50 °C to 90 °C and found the maximum Fe(II) oxidation rate at 70 °C. A similar temperature range (65 °C to 80 °C) on the identical system was explored in another study [115], and the reaction rate was found to increase slightly with temperature. Zhang *et al.* [153] studied Fe(II) oxidation by SO_2-O_2 from 40 °C to 95 °C and found the rate to be the fastest at around 80 °C. The presence of an optimal temperature on Fe(II) oxidation rate has been interpreted as a balance point between the kinetic benefit of higher temperature and the disbenefit of reduced O_2 solubility (see A1 in Appendix A).

5.2.7 Ionic effect—ionic strength. Generally, oxidation rate tends to decline with higher ionic strength [150, 154–160]. The rate-retarding effect imposed by ions may be understood at two levels. The primary ionic effect is non-ionic specific. Stronger ionic interaction in the aqueous phase alter the activities of reactive species, ultimately affecting the reaction rate. The primary ionic effect can be appropriately accounted for with ionic-strength corrected activity coefficients.

The secondary ionic effect is the species-specific influence due to physicochemical nature of the particular ions. In Fe-S(IV)-O_2 system, anions can bind to the catalytically active Fe(III) and form complexes. Anions such as Cl^- or NO_3^- are very labile and co-ordinate to Fe(III) rather weakly. However, chelators such as oxalate ($C_2O_4^{2-}$) bind strongly to Fe(III) and so may lessen or even inhibit its redox-catalytic capacity. Anions such as carboxylates may also act as radical scavengers, which have been demonstrated to interfere with the Fe(III)-S(IV) induced redox chemistry in various way [49, 161–163] (section 5.4.2). Anions like oxalate can act as strong-binding ligand and as radical scavenger while Cl^- and NO_3^- are relative poor in both.

Non-Fe cations may also exert secondary effects depending on their chemical nature and relative abundance. Non-transition metal ions such as Ca^{2+} and Mg^{2+} have been found to lower S(IV) oxidation [164]. Although they are poor co-ordination centers (i.e. small $\log \beta$) [79, 81], at high concentrations they may control Fe and S(IV) speciations, thereby altering the concentrations of rate determining complexes in Fe-S(IV)-O_2 system. Non-Fe transition metal ions with reduced valencies have also been reported to inhibit Fe(II) or S(IV) oxidation to some extent (see section 5.4.4).

5.2.8 Ionic effect—ion-specific effects. Millero [159] investigated the effects of specific ions on Fe(II) oxidation by O_2. At constant pH and ionic strength, the rate was found to vary with anion type, with the oxidation of Fe(II) to be fastest in the presence of HCO_3^-, followed in descending order by Br^-, ClO_4^-, NO_3^-, Cl^-, and SO_4^{2-}. The observed ion-specific effect on rate was explained by the varying strength of interactions between the anions and Fe(II).

The rate-retarding effect of sulphate on catalytic S(IV) oxidation has been attributed to it complexing with Fe(II). Martin [64] suggested that Fe(II) and S(IV) form a complex that was sufficiently stable to resist oxidation by either O_2 or H_2O_2. Considering the comparable rate of H_2O_2 and HSO_5^- induced S(IV) oxidation [165], it may be inferred that the complex would also resist oxidation by HSO_5^-. Huss *et al.* [98, 150] also observed similar inhibitive effect of sulphate on SO_2 oxidation in the presence of Fe(II) and likewise explained the phenomenon with the stability of $FeSO_4$ complex. By similar argument, Cho [142] had stressed the importance of uncomplexed free metal ion concentrations in kinetic calculations and suggested that the formation of all Fe(II)- and Fe(III)-S(VI) complexes be accounted for. Iwai *et al.* [149] studied Fe(II) oxidation by O_2 in sulphuric acid and observed that H_2SO_4 had no effect on the rate constant beyond 1 M. This may suggest oxidation of Fe(II) takes place even as $Fe^{II}SO_4$.

Catalysis of S(IV) oxidation due to Cl^- has been reported in acidic to near neutral pH range [156, 157, 166]. This may be due to the formation of $Cl_2^{\bullet-}$, which then induces S(IV) oxidation via a radical pathway. Similar halogen molecule radicals have been found to react readily with S(IV) (see C1 in Appendix C) in atmospheric systems.

The specific effects of other ions and compounds are covered in section 5.4.

5.2.9 Aging effect. The rate of S(IV) auto-oxidation under Fe(III) catalysis generally decreases with aging (i.e. hydration time of Fe(III)). The concentration of $FeOH^{2+}$, which is one of the catalytically active forms of Fe(III), may change depending on the age of the solution [167]. Novič *et al.* [168] studied S(IV) oxidation rate by adding S(IV) to Fe(III) solution after different hydration times and found the rate slowed down when S(IV) was added later. Reduced catalytic activity due to aging of Fe(III) solution was also observed by Brandt *et al.* [94]. Although they attributed the lowered oxidation rate to the formation of dimeric and polymeric Fe(III)-hydroxo species (i.e., $Fe_m^{III}(OH)_n^{(3m-n)+}$, m, n $\geq$ 2), their rate data showed that the S(IV) oxidation rate constant was essentially constant over the first 2 hrs. Considering the formation of dinuclear Fe(III)-hydroxo species happens within sub-second timescales (section 5.1.2), the claim was not well supported. The results from both studies were consistent with the polymerization theory in a previous review [100].

5.3 *Catalytic synergism in Fe-S(IV)-O_2 system*

It has been observed that when more than one transition metal ion is present in the aqueous solution, the rate of S(IV) autoxidation could be promoted to a level greater than the sum of the rate of reactions catalyzed by individual metal ions. The most studied and recognized synergistic system for S(IV) autoxidation was that catalyzed by Fe and Mn, in particular Fe(III)-Mn(II) [51, 64, 112, 147, 169–171] and Fe(III)-Cu(II) [119, 131, 170]. However, no synergism was reported for Fe(III)-Mn(II) by [131] nor Fe(III)-Cu(II) by [64]. The synergism of other Fe-Me pairs are more disputable. Brandt [171] observed catalytic synergism in Fe(III) induced S(IV) auto-oxidation when Co(II), Ni(II), Cr(III) were present, though others have observed no synergism in their presence [64, 131]. Others reported Fe-Me synergistic pairs are Fe(II)-Mn(II), Fe(III)-Mn(II)-Pb(II) [51, 172] and Fe(II)-Cu(II) [4, 75]. Non-Fe catalytic synergistic combinations can be found in [26, 173].

Catalytic synergism may be conceptually understood as the participating metal ions mutually reinforcing the redox-catalysis that results in an enhanced overall reaction rate exceeding that expected from individual catalysis. Grgić *et al.* [51] proposed that Fe(III)-Mn(II) catalytic synergism could be understood through the coupling of the individual redox cycling mechanisms into one. Mn(II) is first oxidised by Fe(III) to Mn(III). Since Mn(III) could oxidise S(IV) much faster than Fe(III) [76], $SO_3^{\bullet -}$ (or $HSO_3^{\bullet}$) radicals are rapidly formed when S(IV) reacted with Mn(III). The resulting radicals then regenerate Fe(III) from Fe(II), quickly branching up the propagation rate of oxidative intermediates such as $SO_5^{\bullet -}$, $SO_4^{\bullet -}$, and HSO_5^-. The cross-cycling of redox catalysts is completed when the regenerated Fe(III) oxidised more Mn(II) to Mn(III).

But catalytic synergism is not always exhibited in a synergistic pair. This is due to the fact that a synergistic catalysts pair generally consists of a metal catalyst in a relatively oxidised state (e.g., Fe(III)), while the other catalyst is in its reduced state (e.g., Mn(II)). Thus if the reductive catalyst is controlling, the onset of catalytic synergism will be delayed or even halted. For instance, Tiwari *et al.* [4] found that a small amount of Cu^{2+} (1 g/L) could increase the rate of Fe(II) oxidation in the presence of SO_2-O_2. However, at $[Cu^{2+}] \geq 10\,g/L$, the oxidation rate of Fe(II) began to decline. Zhang *et al.* [75] investigated the effect of Cu^{2+} on both the oxidation of Fe(II) by O_2 alone and that by SO_2-O_2 gas mixture. They found that while the presence of Cu^{2+} increased the rate in pure O_2, it produced an inhibiting effect on Fe(II) oxidation in the SO_2-O_2 case. It was suggested that CuO_2^+ and H_2O_2 were formed and they promoted Fe(II) oxidation by pure O_2. In the case of SO_2-O_2, Cu^{2+} acted as an inhibitor of the free radical chain. The supporting evidence for the conclusions was that hydroquinone, a free radical scavenger, inhibited the oxidation of Fe(II) by SO_2-O_2, while the rate of the pure O_2 case was unaffected.

The extent or even presence of a synergistic effect depends upon factors such as the ratio of catalyst concentrations, pH, the initial valence state of metal ions, and whether organic molecules that may act as complexing agent or inhibitor are present [26, 64, 147, 172].

5.4 *Catalytic inhibitionin Fe-S(IV)-O_2 system*

As early as the 1910′s, compounds such as alcohols and aldehydes have been shown to inhibit transition metal catalyzed S(IV) oxidation by O_2 [1]. Numerous studies have shown that catalytic S(IV) auto-oxidation can be slowed down or even stopped when certain organic molecules, known as inhibitors, are present [6, 38, 39, 48, 49, 116, 161–163, 174–179]. These inhibitors reduce the speed and extent of the metal catalyzed S(IV) oxidation in primarily four ways [67, 180, 181]: 1) by deactivating the metal catalyst(s) through strong complexation, 2) by acting as radical scavenging agents, 3) by forming stable adducts with S(IV) oxides, and 4) by acting as competing reductants.

5.4.1 Inhibition due to chelators. Chelating agents such as oxalate [134, 180–183], acetate/formate [67, 181, 184], EDTA [77, 121, 185, 186–188], phenanthroline [116, 189, 190] can bind strongly to metal catalysts and reduce their catalytic activities. Complexed metal centers may interact less readily with S(IV) and other species due to constrained electronic structure and/or steric hindrance from the binding ligands. The redox potential of the metal center may be altered by associated ligands [191, 192], and hence change its tendency to participate in an electron transfer reaction (equation (12)).

$$Fe^{3+} + S(IV) + L^{w-} \longrightarrow FeL_{inactive}^{(3-w)+} + S(IV) \qquad (12)$$

Chelating agents also influence the redox speed by inactivating the reduced Fe(II). Grgić *et al.* [180] observed the onset, duration, and stability of Fe(II) levels to be prolonged and stabilized in the presence of oxalate, suggesting Fe(II) may also be shielded from oxidants in the presence of strong chelators (equation (13)).

$$\mathrm{Fe^{2+} + L^{w-} + oxidant \longrightarrow FeL^{(2-w)+}_{inactive} + oxidant} \tag{13}$$

5.4.2 Inhibition due to radical scavengers.

Radical scavengers are compounds with electron-rich structures such as C π-bonds, aromatic rings, conjugated dienes, or hydroxyl groups which allow them to react readily with radicals. Radicals react with the electron rich structures most frequently by addition (bonding to the structure) or H-abstraction (convert the scavenger into a radical by H-removal) [80]. Their interrupting effect on the free radical chain can be observed at relatively dilute levels (10^{-6} to 10^{-4} M) [49, 161, 178]. Some commonly reported radical scavengers are alcohols [49, 55, 193–195], phenols [58, 112, 161, 196], hydroquinones [161, 197, 198], aromatic amines [198], benzenes [198–200], alkenes [178, 179, 201], carboxylates [58, 202], saccharides, indoles, and amides [161].

The actions of a generic radical scavenger (HIN) on oxysulphur radicals ($\mathrm{SO_X^{\bullet-}}$, X = 3−5), which have been proposed as key reactive oxidants in Me^{n+}-S(IV)-O$_2$ system (see section 6.1.1), are shown in equations (14)–(17). If HIN has good resonance structure, its radical form will be relatively stable, and so it can only react with another radical [162].

$$\mathrm{SO_X^{\bullet-} + HIN \longrightarrow SO_X^{2-} + {}^{\bullet}IN + H^+} \tag{14}$$

$$\mathrm{SO_X^{\bullet-} + OH^- \longrightarrow SO_X^{2-} + {}^{\bullet}OH} \tag{15}$$

$$\mathrm{{}^{\bullet}OH + HIN \longrightarrow H_2O + {}^{\bullet}IN} \quad [\textit{H-abstraction}][203] \tag{16}$$

$$\mathrm{{}^{\bullet}OH + HIN \longrightarrow {}^{\bullet}IN\text{-}OH + H^+} \quad [\textit{addition}][203] \tag{17}$$

5.4.3 Inhibition due to C-S(IV) adducts formation.

Inhibitors may also interrupt S(IV) oxidation by forming stable adducts with S(IV) ions. Aldehydes, for example, have been shown to inhibit S(IV) oxidation in this manner [177, 204]. Well known examples of this group are aldehydes, which are found in atmospheric waters [174, 204, 205], and α-keto acids [161, 174, 175, 177, 206]. Adducts are formed through nucleophilic attack on the carbonyl carbon, with S in S(IV) as nucleophile. The formation reactions are shown in equations (18) and (19) [207].

$$\mathrm{:SO_3^{2-} + RCHO \longrightarrow RCHO^-\text{-}SO_3^-} \tag{18}$$

$$\mathrm{H:SO_3^- + RCHO \longrightarrow RCHO^-\text{-}SO_3} \tag{19}$$

5.4.4 Inhibition due to competing reductants.

Competing reductants include not only reduced organic molecules but also low valence transition metal ions. Ions such as Cr(III), Cu(II), and V(V) have been reported to exhibit inhibitory effects on catalytic S(IV) oxidation as well [4, 75, 151]. The inhibitive action of low valence metal ions are shown in equation (20).

$$\mathrm{Fe(II) + Me^{n+} + SO_X^{\bullet-} \longrightarrow Fe(II) + Me^{(n+1)+} + SO_X^{2-}} \tag{20}$$

Reduced transition metal ions will compete with Fe(II) or S(IV) in getting oxidised, but the long term effect may be catalytic rather than inhibitory. If the overall system is on the oxidative side, the inhibitory effect of reduced metal ions would simply be an induction period, after which S(IV) or Fe(II) oxidation proceeds even much faster due to Fe-Me catalytic synergism (see section 5.3).

5.4.5 Unusual catalytic oxidation induced by inhibitors.

Recently, a number of organic inhibitors were found to exhibit catalytic, rather than inhibitive, effect on S(IV) oxidation at certain conditions. Terpenic derivatives such as cis-verbenol, and nopol [49]; phenol and gallic acid [176] were found to promote S(IV) oxidation when they are present at levels comparable to [Fe(III)]. Phenol, on the other hand, first promoted S(IV) oxidation, but then caused the rate to decay sharply at a later time.

Two radical mechanisms were proposed by Pasiuk-Bronikowska *et al.* [162, 176] to explain the switching of these inhibitors from negative to positive catalysis. The proposed model invokes the presence of monomeric and complex organo-radicals, $A^\bullet$ and $(HAA^\bullet)$, to qualitatively explain the kinetic behaviour of catalytic S(IV) in the presence of gallic acid equations (21)–(25) and phenol (equation (26) followed by equations (21)–(25)).

$$AH + SO_4^{\bullet-} \longrightarrow A^\bullet + HSO_4^- \tag{21}$$

$$A^\bullet + HSO_3^- \longrightarrow AH + SO_3^\bullet \tag{22}$$

$$A^\bullet + AH \longrightarrow (HAA^\bullet) \tag{23}$$

$$(HAA^\bullet) + SO_3^{\bullet-} \longrightarrow \text{inerts} \tag{24}$$

$$2(HAA^\bullet) \longrightarrow \text{inerts} \tag{25}$$

The second mechanism starts with a phenol-metal interaction equation (26), with the remaining reactions identical with equations (21)–(25):

$$Me(III) + AH \longrightarrow Me(II) + A^\bullet + H^+ \tag{26}$$

The dimeric or complex organo-radicals ($AAH^\bullet$ or $AA^\bullet$) are weakly reactive and participate in only recombination reactions with other radicals, while the mono-radical ($A^\bullet$) is still reactive enough to attack non-radical species (e.g., (22), (23)).

Although the general organo-radical based mechanisms qualitatively explain the catalytic function observed for certain compounds, specific kinetic behaviour still needs more elaboration. For instance, when gallic acid was added to Fe(III)dCo(II)-S(IV)-O_2 system, the compound first inhibited catalytic S(IV) oxidation [176]. S(IV) oxidation proceeded at a stable rate for $> \sim 1$ hr. After a long time (~ 2 hr), S(IV) oxidation rate began to change, oscillating between periods of enhanced and steady conversion rates. The mechanism consisting of equations (21)–(25) cannot sufficiently explain such kinetic behaviour.

5.5 *Kinetics in Fe-S(IV)-O_2 system*

A compilation of kinetic expressions from some studies relevant to Fe-S(IV)-O_2 system has been provided in C9 in Appendix C. The list is by no means comprehensive. It is given here to illustrate the greatly varied order of dependence on the concentrations of key redox species and H^+, and the disagreement within experiments conducted at similar/same conditions.

Space limitation does not permit an in-depth discussion on theoretical kinetic expressions for different mechanisms. In 2003, Yermakov and Purmal published an ambitious review [66] with the hope to resolve a number of key mechanistic riddles that have been raised in the past Fe-S(IV)-O_2 studies. There, they offered a systematic and vigorous kinetic analysis on the catalytic redox behaviour from the perspective of oxysulphur radicals chain mechanism. A more accessible formulation of a generalized rate expression involving Fe, S(IV), and O_2 can be found in reviews by Hoffmann *et al.* [112, 208].

5.6 E_H *of Fe-S(IV)-O_2 system*

The E_H of Fe-S(IV)-O_2 and related metal catalysis systems has not been extensively studied, although its peculiarity has been documented. S(IV) is itself a reducing species, but when it is present in aqueous environment together with Fe(III) and $O_{2(aq)}$, the overall system E_H can be promoted to levels as high as or even exceeding the oxidation-reduction potential of the O_2-H_2O couple.

5.6.1 Species contributing to high E_H. Devuyst *et al.* [132] studied the S(IV) oxidation by air in deionized water possibly contaminated with trace levels of metal impurities. They found the solution Eh increased beyond that of the O_2-H_2O couple at around pH 9 and observed the production of an unknown oxidant to increase with the E_H. The observed oxidant could be stable for several hours and was reported to decompose rapidly to some gas, suspected to be O_2 or H_2O_2, upon the addition of $Ca(OH)_2$. Because K_2SO_5 was found to undergo similar decomposition under alkaline condition upon addition of $Ca(OH)_2$, it was suggested that the oxidant was some kind of 'activated complexes' of the form $MeSO_5^{(n-2)}$, with SO_5^{2-} accounting for the high oxidation potential observed at elevated pH.

In another Fe(III)-$SO_{2(g)}$-$O_{2(g)}$ study, Zhang *et al.* [153] likewise reported unusually high E_H, but at low pH (1–3). In the absence of SO_2, the system E_H, however, was always below the O_2-H_2O boundary. The observed E_H with SO_2-O_2 input was claimed to be similar to the oxidation potential of HSO_5^-/HSO_4^- and that of H_2SO_5 hydrolysis. HSO_3^- was claimed to be the reactive form based on the observation that high E_H did not occur at $pH < 0.5 < pK_a(H_2O.SO_2)$, where the oxidation rate was slow. The maximum E_H increased linearly with [Fe(III)] up to 0.03 M and then became independent beyond that concentration.

5.6.2 Response of E_H to system parameters. Recently, Kuo [209] investigated the behaviour of E_H in an aqueous Fe-S(IV)-O_2 system in response to [Fe(III)], [S(IV)], O_2, mixing rate, pH, and glucose (as a reductant). The E_H levels over 1.3 V were attained only when Fe(III), S(IV) and $O_{2(aq)}$ were all present and when sufficient mixing was applied. Furthermore, the E_H of the system could be manipulated reversibly between the plus-1.3 V (hyper-E_H) and the sub-0.9 V (hypo-E_H) levels by addition of S(IV) at different amounts and frequencies. The effect of mixing and observation at different [S(IV)]/[Fe(III)] ratios led to the hypothesis that the local [S(IV)]/[Fe(III)] was critical to the response of the system E_H. Stepwise S(IV) addition experiment showed that the plus-1.3 V levels could be achieved at $[S(IV)]_o/[Fe(III)] < 1$. The system pH affected the response rate of E_H to S(IV) injection, but not the maximum attainable value.

The presence of glucose, even at a trace level (3.5×10^{-7} M), seem prevented the system from reaching the plus-1.3 V levels. The maximum E_H attained by the system decreased as the concentration of glucose increased. Evolution of gas was not observed, implying glucose did not mineralize to CO_2.

5.6.3 The meaning of measured E_H in Fe-S(IV)-O_2 system. The meaning of the reported hyper-E_H remains unclear. Zhang *et al.* [75] claimed the high E_H they observed after 30 minutes was the equilibrium system E_H, without showing any E_H-time plots. This is inconsistent with the observation by Kuo [209], where Eh was found to change with time, and more importantly, with the addition of S(IV). Moreover, given O_2 as the ultimate oxidant, the equilibrium E_H should not exceed that of the O_2-H_2O.

Zhang *et al.* [75] also attributed the high E_H to SO_5^{2-} with reference to a similar observation made by Devuyst *et al.* [132]. However, their system was at low pH (0–3) while that investigated by Devuyst *et al.* was in the alkaline range (pH > 9). $Ca(OH)_2$ addition to one sample with plus-1.3 V E_H revealed no gas formation, suggesting either the complete absence of SO_5^{2-} in the solution, or that its concentration was undetectable [209]. The potential of $SO_5^{\bullet-}$ is expected to be around 1.4 V at pH 2, and 0.9 V at pH > 10 [58]. The high E_H (~1.4 V) has been shown to be highly stable for more than 10 hrs [132, 209]. How could the relatively stable E_H be reconciled with highly reactive species such as $SO_5^{\bullet-}$ or SO_5^{2-}? Or could the system be at E_H disequilibrium [31]?

6. Mechanisms of redox reactions in aqueous Fe-S(IV)-O_2 system

Any feasible, valid mechanism for the Fe catalysis of S(IV) (or other reductants) oxidation must at least be able to explain: 1) the 'catalytic' or induced redox chemistry involving Fe-S(IV) interactions in the presence of O_2, 2) the co-oxidation of Fe(II) and S(IV) to Fe(III) and S(VI), under sufficient O_2 supply and appropriate [Fe(III)]/[S(IV)] ratio, 3) the catalytic synergism on S(IV) or Fe(II) oxidation in the presence of other transition metal ions, and 4) the overall redox behaviour in the presence of inhibitors.

6.1 *Mechanisms for redox reactions in pure aqueous Fe-S(IV)-O_2*

The mechanisms proposed for the reactions in Fe-S(IV)-$O_{2(aq)}$ system can be divided into three categories: (a) free radicals based mechanism, (b) inner-sphere electron transfer mechanism within Fe-sulphito complexes, and (c) mixed mechanisms of (a) and (b) [26, 77]. All three categories recognize the formation of some Fe-S(IV) complexes as the first step of the reaction network. The radicals based and the electron transfer mechanisms differ primarily in the account of the subsequent reactions undertaken by the Fe-S(IV) complexes.

6.2 *Free radical chain mechanism—oxysulphur radicals*

The oxysulphur radicals chain model has been most frequently quoted to explain redox chemistry in Fe-S(IV)-O_2 system. First proposed by Backström [210] and later modified by Haber [211] to the current framework, the model essentially suggests Fe(III)-S(IV) complex(es) decomposes to produce $SO_3^{\bullet-}$, which eventually leads to the formation of other oxidative oxysulphur intermediates ($SO_4^{\bullet-}$, $SO_5^{\bullet-}$, HSO_5^-, and SO_5^{2-}) in the presence of O_2. These highly oxidative oxysulphur species are responsible for the rapid oxidation of reductants, such as S(IV) or organic species, as well as the regeneration of Fe(III). The oxysulphur radical chain mechanism has been widely supported and favoured for it can best explain the rapid auto-oxidation of S(IV) [75, 76, 114, 212, 213] and the inhibitory effects of organic molecules with radical scavenging capability [48, 161, 163, 214].

6.2.1 Oxysulphur radicals mechanism—radical initiation phase. The mechanism can be divided into three phases: initiation, propagation, and termination. The initiation phase begins with the formation of Fe(III)-S(IV) complex(es) (equation (27)), which undergoes an intra-complex single electron transfer to produce $SO_3^{\bullet-}$ (equation (28)).

$$SO_3^{2-} + Fe^{3+} \longleftrightarrow Fe^{III}SO_3^+ \quad [\textit{fast}] \tag{27}$$

$$Fe^{III}SO_3^+ \longrightarrow Fe^{2+} + SO_3^{\bullet-} \quad [\textit{rate limiting step}] \tag{28}$$

The rate limiting step for the entire reaction network depends on the how fast Fe-S(IV) complex(es) decays, via thermolysis, to yield $SO_3^{\bullet -}$. Various Fe-S(IV) complexes have been claimed to be the key $SO_3^{\bullet -}$ yielding complex. Kraft *et al.* [73] and Lente *et al.* [45] claimed that $Fe^{III}SO_3^+$ (i.e. equation (28)) was the rate determining Fe(III) complex based on early microsecond scale observations. Brandt *et al.* [114], suggested in a scheme that mono-Fe(III) center complexes of the generic form $Fe^{III}(HSO_3^-)_n^{(3-n)+}$ may be controlling the overall rate. Ziajka *et al.* [214] and Reddy *et al.* [133] believed the rate limiting complex was $Fe(OH)(SO_3H)^+$, formed from the co-ordination of $FeOH^{2+} + HSO_3^-$. Yermakov *et al.* [215] also favoured $Fe(OH)(SO_3H)^+$ over the other Fe-S(IV) complexes as rate determining in their modeling analysis, though no specific reasons were provided for the choice.

An alternative initiation path (equations (29)–(31)) was proposed by Martin *et al.* [67] with $Fe_2^{III}(OH)_4^{2+}$ as the rate determining complex that decays to release $^\bullet OH$:

$$2Fe^{III}(OH)_2^+ \longleftrightarrow Fe_2^{III}(OH)_4^{2+} \tag{29}$$

$$Fe_2^{III}(OH)_4^{2+} + OH^- \longrightarrow {}^\bullet OH + Fe^{II}(OH)_2 + Fe^{III}(OH)_2^+ \tag{30}$$

$$HSO_3^- + {}^\bullet OH \longrightarrow H_2O + SO_3^{\bullet -} \tag{31}$$

Brandt *et al.* [94] studied the effect of solution aging on Fe(III) catalyzed S(IV) oxidation and found that the catalytic activity of Fe(III) decayed with aging. The reduced catalytic was attributed to the formation of dimeric and polymer Fe(III)-hydroxo species. However, their rate data showed that S(IV) oxidation rate constant was essentially constant over the first 2 hrs. Since $Fe_2^{III}(OH)_4^{2+}$ is formed in sub-second scale (see section 5.1.2), one may not conclusively claim that the dimeric Fe(III)-hydroxo complex is catalytically insignificant. However, Lente *et al.* [45] rejected another dimeric candidate, $Fe_2(OH)SO_3^{3+}$, as an important contributor in the initiation phase based on a model fitting argument.

6.2.2 Oxysulphur radicals mechanism—radical propagation phase. The propagation phase begins with rapid reaction between $SO_3^{\bullet -}$ and O_2 to form $SO_5^{\bullet -}$ (equation (32)), which in turn leads to the formation of other reactive oxysulphur intermediates (equations (33)–(35)).

$$SO_3^{\bullet -} + O_2 \longrightarrow SO_5^{\bullet -} \tag{32}$$

$$SO_5^{\bullet -} + SO_3^{2-} \longrightarrow SO_5^{2-} + SO_3^{\bullet -} \tag{33}$$

$$SO_5^{\bullet -} + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_4^{\bullet -} \tag{34}$$

$$SO_4^{\bullet -} + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^{\bullet -} \tag{35}$$

$$Fe^{2+} + SO_5^{\bullet -} \longrightarrow Fe^{3+} + SO_5^{2-} \tag{36}$$

$$Fe^{2+} + SO_5^{2-} + H^+ \longrightarrow Fe^{3+} + SO_4^{\bullet -} + OH^- \tag{37}$$

$$Fe^{2+} + SO_4^{\bullet -} \longrightarrow Fe^{3+} + SO_4^{2-} \tag{38}$$

Fe(III) is regenerated by the reactive oxysulphur intermediates via equations (36)–(38). Chain branching occurs in equation (36) and equation (37) because the restoration of Fe(III) is accompanied by the additional formation of oxysulphur oxidants ($SO_5^{\bullet -}$, SO_5^{2-}). An important refinement on the radical mechanism was the inclusion of Caro's acid (HSO_5^-) into the main mechanism [55, 118, 379] because it adds a new branching pathway [66]. The reactive chain primarily ends via radical recombination (equations (39) and (40)):

$$2SO_5^{\bullet -} \longrightarrow S_2O_8^{2-} + O_2 \tag{39}$$

$$SO_5^{2-} + SO_3^{2-} \longrightarrow 2SO_4^{2-} \tag{40}$$

6.2.3 Oxysulphur radicals mechanism—radical termination phase. Equations (27), (28) and (32–40) represent the core, simplified elementary reactions in the oxysulphur radical chain model. They can be easily found in literature [26, 27, 59, 60, 66, 114, 210]. In reality, each reaction may proceed with the reactants in combinations of protonated or deprotonated form. It is important to realize the kinetics can be very different for protonated vs deprotonated reactants (see C1 to C5 in Appendix C).

6.2.4 Oxysulphur radicals mechanism—additional reactions. Hoffmann and Jacob [112] suggested three more reactions to reinforce the formation of dithionate (equations (41)–(43)).

$$2SO_3^{\bullet -} \longrightarrow S_2O_6^{2-} \tag{41}$$

$$SO_3^{\bullet -} + SO_5^{\bullet -} \longrightarrow S_2O_6^{2-} + O_2 \tag{42}$$

$$2SO_5^{\bullet -} \longrightarrow S_2O_6^{2-} + 2O_2 \tag{43}$$

$^\bullet$OH generation during the propagation phase (equation (44)), its role in Fe(III) regeneration (equation (45)), as well as Fe(III) by $SO_3^{\bullet -}$ (equation (46)), have been considered by Brandt *et al.* [114].

$$Fe^{2+} + SO_5^{2-} + H^+ \longrightarrow Fe^{3+} + SO_4^{2-} + {}^\bullet OH \tag{44}$$

$$Fe^{2+} + {}^\bullet OH + H^+ \longrightarrow Fe^{3+} + H_2O \tag{45}$$

$$Fe^{2+} + SO_3^{\bullet -} + OH^- \longrightarrow Fe^{3+} + SO_4^{2-} + H^+ \tag{46}$$

Based upon the discovery of $S_2O_7^{2-}$ formation in non-catalytic S(IV) oxidation by Chang *et al.* [120], Connick *et al.* [121, 216] reported the extent of $S_2O_7^{2-}$ production by titration technique. They believed as much as 90% of sulphate form via equation (40) came from $S_2O_7^{2-}$ hydrolysis [216], and that it was an important S(VI) intermediate in non-catalytic oxidation of S(IV). The following scheme involving $S_2O_7^{2-}$ was suggested (equations (47)–(50)) [216, 217]:

$$SO_2 + HSO_5^- \longrightarrow O_3SOOSO_2^{2-} + H^+ \tag{47}$$

$$HSO_3^- + HSO_5^- \longleftrightarrow O_3SOOSO_2^{2-} + H_2O \tag{48}$$

$$O_3SOOSO_2^{2-} \longrightarrow O_3SOSO_3^{2-} \tag{49}$$

$$O_3SOSO_3^{2-} + H_2O \longrightarrow 2SO_4^{2-} + 2H^+ \tag{50}$$

6.2.5 Oxysulphur radicals mechanism—other variations. Variation on the oxysulphur radicals chain mechanism can be found. For instance, Karraker [212] proposed a mechanism involving $SO_3^{\bullet -}$ and H_2O_2.

$$Fe^{3+} + H_2O{\cdot}SO_{2(aq)} \longrightarrow Fe^{2+} + HSO_3^\bullet + H^+ \tag{51}$$

$$HSO_3^\bullet + O_2 + H_2O \longrightarrow SO_4^{2-} + HO_2^\bullet + 2H^+ \tag{52}$$

$$\mathrm{Fe^{2+} + HO_2^{\bullet} + H^+ \longrightarrow Fe^{3+} + H_2O_2} \tag{53}$$

$$\mathrm{Fe^{2+} + H_2O_2 + H^+ \longrightarrow Fe^{3+} + {}^{\bullet}OH + H_2O} \tag{54}$$

$$\mathrm{HSO_3^{\bullet} + {}^{\bullet}OH \longrightarrow SO_4^{2-} + 2H^+} \tag{55}$$

According to the mechanism, Fe(III) was regenerated by Fenton's reaction (equations (53) and (54)) [218], while equations (52) and (55) were the two paths for sulphate production. Equation (55) is likely to be insignificant, because $^{\bullet}$OH production from equation (54) is rather slow ($k \sim 60\,\mathrm{M^{-1}s^{-1}}$, see C4 in Appendix C), and both [$\mathrm{HSO_3^{\bullet}}$] and [$^{\bullet}$OH] are expected to be very low. Equation (52) can be re-expressed essentially as the formation of $\mathrm{SO_5^{\bullet-}}$ and its hydrolytic decay into sulphate and $\mathrm{HO_2^{\bullet}}$. Based on kinetic considerations, this mechanism seems to be, at best, a minor one in comparison to the classical oxysulphur radicals pathway.

6.3 *Fe-sulphito complex mediated mechanisms*

This mechanism suggests that transfer of electrons is facilitated in the presence of Fe-sulphito complexes. In the context of Fe-S(IV)-$\mathrm{O_2}$ redox chemistry, S(IV) oxidation proceeds in the Fe-bound form, where two electrons are shuttled from S(IV) to oxygen through inner-sphere transfer. Oxysulphur radicals and intermediates are absent in this mechanism category. However, powerful oxidants such as $\mathrm{H_2O_2}$ may be produced as a result of the decay of Fe-S(IV) complexes and be responsible for the rapid redox reactions. The earliest proponent for the complex mediated mechanism was Bassett and Parker [154]. It has been adopted by Freiberg [219], Cho [142], Conklin and Hoffmann [72, 136], Kao [220], Kraft *et al.* [73], and Krause [74] to explain kinetic observations in Fe-S(IV)-$\mathrm{O_2}$ or related systems. Due to the absence of a core reaction network, different models would be covered individually.

6.3.1 Complex mediated mechanism—$\mathbf{Fe^{III}(HSO_3)(SO_3)}$. Freiberg [219] proposed $\mathrm{Fe(HSO_3)(SO_3)}$ as the key Fe-sulphito complex in the rate determining step of S(IV) autoxidation (equations (56)–(59)).

$$\mathrm{Fe^{3+} + HSO_3^- \longleftrightarrow Fe^{III}(HSO_3)^{2+}} \tag{56}$$

$$\mathrm{Fe^{III}(HSO_3)^{2+} + SO_3^{2-} \longleftrightarrow Fe^{III}(HSO_3)(SO_3)} \quad [\textit{rate limiting step}] \tag{57}$$

$$\mathrm{Fe^{III}(HSO_3)(SO_3) + O_2 + H_2O \longrightarrow Fe^{III}(OH)^{2+} + 2HSO_4^{2-}} \tag{58}$$

$$\mathrm{Fe^{III}(HSO_3)(SO_3) + Fe^{3+} + H_2O \longleftrightarrow 2Fe^{2+} + HSO_4^- + HSO_3^- + H^+} \tag{59}$$

Equations (58) and (59) are each likely to be the stochiometric representation of two or more elementary reactions. In equation (58), for example, the complex probably first forms an adduct with $\mathrm{O_2}$, then goes through a number of electron transfer steps, and finally hydrolyzes a water molecule. Unfortunately, the mechanism is incomplete because the regeneration of Fe(III) was not accounted for.

Cho [142] modified the mechanism proposed by Freiberg to obtain better modelling of experimental data. After $\mathrm{Fe^{III}(HSO_3)(SO_3)}$ was formed (equation (57)), three additional pathways for S(IV) oxidation were proposed (equations (60)–(62)):

$$\mathrm{3Fe^{3+} + Fe^{III}(HSO_3)(SO_3) + 2H_2O \longrightarrow 4Fe^{2+} + 2SO_4^{2-} + 5H^+} \tag{60}$$

$$\mathrm{Fe^{III}(HSO_3)(SO_3) + O_2 \longrightarrow Fe^{3+} + 2SO_4^{2-} + H^+} \tag{61}$$

$$\mathrm{2Fe^{2+} + SO_2(aq) + O_2 \longrightarrow 2Fe^{3+} + SO_4^{2-}} \tag{62}$$

Again, equation (62) is likely to consist of more elementary steps involving formation of mono- or di-nuclear Fe(II)-S(IV) complexes and electron transfer steps.

6.3.2 Complex mediated mechanism—$HOFe^{III}\ OS^{IV}O_2$.

Conklin and Hoffmann [136] proposed a complex-based mechanism in which the $HOFe^{III}(O_2^{\bullet -})OS^{V}O_2$ formation was the rate determining step. The Fe(II)-S(V) complex, which was believed to be orange in colour, decayed upon contact with oxygen. S(VI) oxidation could take place through three pathways, including the oxidation by H_2O_2 (equations (63)–(70)).

$$Fe^{3+} + H_2O \longleftrightarrow FeOH^{2+} + H^+ \quad [\textit{fast}] \tag{63}$$

$$FeOH^{2+} + SO_3^{2-} \longleftrightarrow HOFe^{III}OSO_2 \tag{64}$$

$$HOFe^{III}OS^{IV}O_2 \longleftrightarrow HOFe^{II}OS^{V}O_2 \quad [\textit{rate limiting step}] \tag{65}$$

$$HOFe^{II}OS^{V}O_2 + O_2 \longleftrightarrow HOFe^{III}(O_2^{\bullet -})OS^{V}O_2 \tag{66}$$

$$HOFe^{III}(O_2^{\bullet -})OS^{V}O_2 \longrightarrow HOFe^{III}(O_2^{2-})OS^{VI}O_2 \tag{67}$$

$$HOFe^{III}(O_2^{2-})OS^{VI}O_2 + 2H^+ \longrightarrow HOFe^{2+} + SO_3 + H_2O_2 \tag{68}$$

$$SO_3 + H_2O \longrightarrow 2H^+ + SO_4^{2-} \tag{69}$$

$$H_2O_2 + HSO_3^- \longrightarrow H_2O + H^+ + SO_4^{2} \tag{70}$$

The electron transfer step which results in $Fe^{II}S^{V}$ formation (equations (65)) was estimated to have a forward rate constant of about 0.04 s^{-1}.

6.3.3 Complex mediated mechanism—$[Fe^{III}SO_3Fe^{II}]^{3+}$.

Krause [74] proposed a complex-mediated mechanism in which the oxidation of a mixed valence Fe-S(IV) complex was the rate determining step (equations (71)–(74)).

$$Fe^{3+} + HSO_3^- \longleftrightarrow FeSO_3^+ + H^+ \tag{71}$$

$$FeSO_3^+ + Fe^{2+} \longrightarrow [Fe^{III}SO_3Fe^{II}]^{3+} \tag{72}$$

$$[Fe^{III}SO_3Fe^{II}]^{3+} + O_2 \longrightarrow Fe(III), S(IV) \quad [\textit{rate limiting step}] \tag{73}$$

$$2[Fe^{III}SO_3Fe^{II}]^{3+} + H_2O \longrightarrow 4Fe^{2+} + SO_4^{2-} + HSO_3^- + H^+ \tag{74}$$

Under oxic conditions Fe(II) and S(IV) would be oxidised according to equation (73). When oxygen is limiting, the complex would decay as equation (74).

6.3.4 Complex mediated mechanism—$[Fe^{III}(SO_3)_2]^-$.

Based on the work of Joshi *et al.* [221], Kraft *et al.* [73] endorsed a complex mechanism with $[Fe^{III}(SO_3)_2]^-$ as the precursor species for subsequent intra-complex oxidation (equations (75)–(80)).

$$[Fe^{III}(SO_3)_2]^- + O_2 \longrightarrow [(^{\bullet}O_2)Fe^{III}(SO_3)_2]^- \tag{75}$$

$$[(^{\bullet}O_2)Fe^{III}(S^{IV}O_3)_2]^- \longrightarrow [(^{\bullet}O_2)Fe^{II}(S^{IV}O_3)(S^{V}O_3)]^- \tag{76}$$

$$[(^{\bullet}O_2)Fe^{II}(S^{IV}O_3)(S^{V}O_3)]^- \longrightarrow [(^{-}O_2)Fe^{III}(S^{IV}O_3)(S^{V}O_3)]^- \tag{77}$$

$$[(^{-}O_2)Fe^{III}(S^{IV}O_3)(S^{V}O_3)]^- \longrightarrow [(^{-}O_2)Fe^{II}(S^{V}O_3)_2]^- \tag{78}$$

$$[(^{-}O_2)Fe^{II}(S^{V}O_3)_2]^{-} + 2H^{+} \longrightarrow H_2O_2 + Fe^{3+} + S_2O_6^{2-} \tag{79}$$

$$[(^{-}O_2)Fe^{II}(S^{V}O_3)_2]^{-} + H_2O \longrightarrow H_2O_2 + Fe^{3+} + SO_3^{2-} + SO_4^{2-} \tag{80}$$

The formation of an oxo-sulphito complex (equation (75)) was suggested based on the observation of O_2 influencing the Fe-S(IV) absorbance signal prior to the decay phase (phase II in section 5.1.2). Further kinetic and entropic analysis on the decay phase suggested the existence of a relatively well-structured species in agreement with the Fe-sulphito superoxo complex. It was also consistent with the finding of Miksztal *et al.* [222], who demonstrated the mononuclear Fe^{III}-porphyrin peroxo complex, $FeP(O_2^{-})$, was capable of oxidizing S(IV) to form sulphate or sulphito complexes. Equation (79) was proposed to account for the production of dithionate in the presence of O_2.

6.4 *Mixed mechanisms*

Huss *et al.* [150] and Martin *et al.* [67] took a more inclusive approach and suggested that both the oxysulphur radical chain mechanism and the metal-sulphito complex mediated model were at work in different pH regimes. This hypothesis was primarily motivated by their observations of an inhibition effect of organic molecules on S(IV) auto-oxidation [116] and the fact that either mechanism cannot explain kinetic data in a wide pH range [67].

The main evidence for the radicals based mechanism has been the observation of inhibition effect in the presence of organic compounds that are known as radical scavengers (section 5.4). Huss *et al.* [150] suggested that both the radical and the complex-mediated mechanisms were important for Fe(II)-catalyzed oxidation. Lim *et al.* [116] carried out a comprehensive investigation on the inhibition effect of radical scavengers on S(IV) oxidation catalyzed by Mn(II), Fe(II) and Cu(II). They found Mn(II) catalysis was greatly inhibited in the presence of radical scavengers, whereas Fe(II) catalysis was only moderately affected. From this they concluded that the Mn(II) catalysis was essentially mediated via a free-radical chain mechanism, while the Fe(II) catalyzed reaction proceeded through both the radical based and the non-radical based mechanisms. Furthermore, they pointed out radical scavengers could also be oxidised by molecular oxygen, and in the case of hydroquinone, it was mostly oxidised by oxygen rather than by sulphur oxides radicals.

Martin *et al.* [67] studied the Fe(III)-catalyzed S(IV) oxidation. They found that non-complexing organic molecules only significantly inhibited S(IV) auto-oxidation at $pH > 5$, but not at $pH < 3$. This was explained in terms of different mechanism prevailing in different pH regimes. They showed that kinetic data at $pH > 5$ fitted well into a modified radical model. At $pH < 3$, the kinetic observations including particular phenomena such as self-inhibition, sulphate inhibition and ionic strength effect, however, were in agreement with the predictions based on the complex-mediated mechanism. It should be noted that most organic substrates are in the protonated form at low pH [80], and hence have a weak inhibiting effect.

6.5 *Support for each mechanism*

6.5.1 Evidence for oxysulphur radical chain mechanism. There is supportive evidence for the radicals based mechanism. The mechanism is able to explain the rapid catalytic oxidation in the Fe-S(IV)-O_2 system, how both S(IV) and Fe(II) can be oxidised, and how Fe(III) may be regenerated. The mechanism is consistent with the observation of the inhibition effect in the presence of organic radical scavengers [48, 49, 161, 162, 176, 178, 179]. Finally, the mechanism is able to explain the existence of oxysulphur radicals as proven by pulse radiolysis [52, 55] and electron spin resonance [223–225] studies. Thus, all the criteria mentioned in the beginning of this chapter are well met.

6.5.2 Evidence for Fe-S(IV) complex-mediated mechanism. There is supporting evidence for the complex-based mechanism. Model variations such as that described in sections 6.3.2 and 6.3.4 can explain the catalytic oxidation behaviour, including key observations such as Fe(III) regeneration, oxygen as the ultimate electron acceptor. Furthermore, the two models proposed by Conklin *et al.* [136] and Kraft *et al.* [73] were strongly supported by spectroscopic observations, and that the Fe-peroxo structures are confirmed, realistic structures [88, 89, 91, 222].

6.5.3 Comparative discussion on the radical and complex-mediated mechanisms. In both mechanisms, the formation of Fe(III)-S(IV) complexes and the subsequent decomposition are regarded as the key reaction steps. The main disagreement has been how oxygen becomes redox-active through the subsequent transformation steps.

The radical mechanism is superior in that the intrinsic rates of most of the involved reaction steps have been measured [27, 56, 59, 215] and have been used in large scale atmospheric chemistry modeling studies [56, 69, 70]. Recently, Buxton *et al.* [52, 53] estimated the intrinsic rates for oxidation of Fe(II) by $SO_3^{\bullet -}$ and $SO_4^{\bullet -}$, unprecedentedly distinguishing the forward formation rate of $[Fe^{II}SO_3^{\bullet}]^-$ complex, the intra-complex electron transfer rate, and the overall 2nd order rate constant (see C4 in Appendix C). These findings along with the results from inhibition studies, quite convincingly ascertain the oxysulphur-radicals pathway as a valid mechanism for Fe(III) catalyzed S(IV) auto-oxidation in atmospheric systems, where UV radiation and other reactive oxidants such as $^{\bullet}OH$ and H_2O_2 are highly abundant.

However, this does not imply the oxysulphur radical mechanism also prevails under energetically moderate conditions. In laboratory dark-phase studies and industrial processes such as flue gas desulphurization where UV irradiation and highly reactive oxidative species are all absent, the validity of oxysulphur radicals mechanism is highly questionable (see section 7.2).

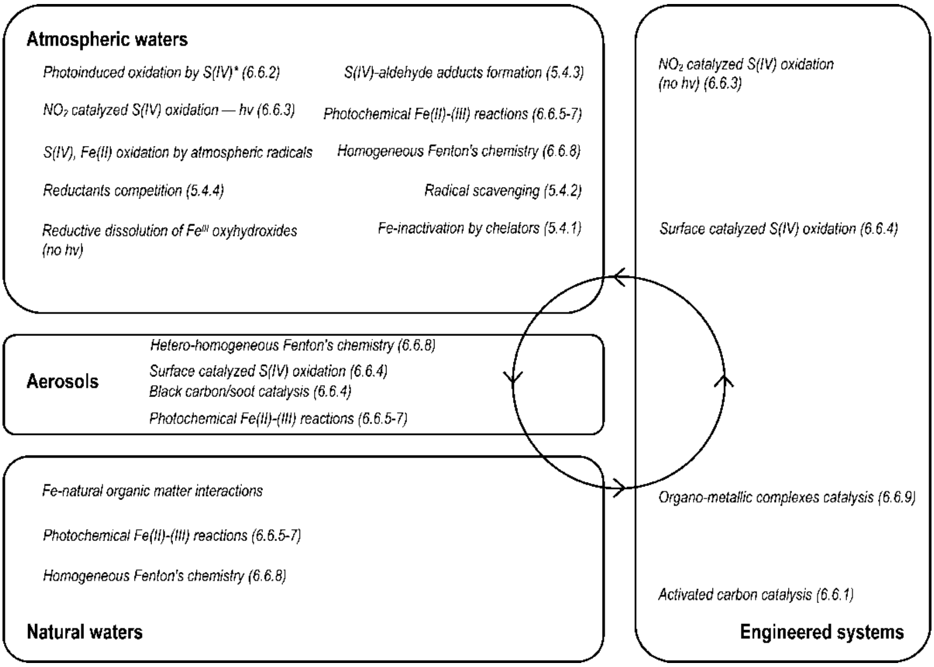
For biochemical phenomena such as S(IV) induced DNA damages, the argument for complex-mediated mechanism should be strong because the role of Fe-peroxo complexes in vital biological structures such as hemoglobin and cytochrome is well established [88, 91, 89].

In cases where large chelators such as tetrasulphphthalocyanine (TSP) are present, S(IV) auto-oxidation via the radical path seems unlikely. Tetra- and penta-coordinated Fe(II) complexes are capable of carrying dioxygen in aqueous system [226, 227]. Boyce *et al.* [77] observed no dithionate ($S_2O_6^{2-}$) formation and insignificant inhibition with addition of mannitol (radical scavenger) in S(IV) oxidation catalyzed by Me-TSP complexes.

Conklin *et al.* [136] successfully developed, in *a priori* without any fitting parameters, a kinetic expression and rate constant that matched kinetic data observed from four other studies, covering pH from $\sim$1.5 to $>$6. They also argued that the kinetic expressions in other studies often conformed poorly to the general expression derived based on radical model [112, 208], in particular the reaction order of specific reactant. Furthermore, although the formation kinetics of Fe(III)-S(IV) complexes has no O_2 dependence [45, 73], the decay kinetics can be influenced by its presence [73]. In the radical model, the formation of $SO_3^{\bullet -}$ from $FeSO_3^+$ is the rate limiting step in S(IV) auto-oxidation, which O_2 is neither involved with nor limiting (for $SO_3^{\bullet -} + O_2 \rightarrow SO_5^{\bullet -}, k \sim 10^9\ M^{-1}\ s^{-1}$).

6.6 *Fe-S(IV)-O_2 in the context of natural processes and engineered systems (scheme 4)*

6.6.1 Activated carbon catalyzed S(IV) oxidation. A number of studies have looked into S(IV) oxidation catalyzed by activated carbon (AC) slurries [14, 228–230]. In the 1970's, Komiyama *et al.* [230] reported accelerated SO_2 oxidation in AC slurries. Fu *et al.* [228] compared the S(IV) oxidation catalyzed by AC (heterogeneous) and by Co(II) (homogeneous),



SCHEME 4 Fe-S(IV)-O_2 in the context of natural processes and engineered systems.

and found that in the low pH regime (~2–3), the heterogeneous catalysis dominated, while the homogeneous catalysis took over at pH 7–8. The rate determining step was suggested to be the exchange reaction between adsorbed O_2 and S(IV).

Govindarao *et al.* [229] proposed a mechanism for AC catalytic S(IV) oxidation in low pH regime. They suggested that HSO_3^- and $H_2O^\bullet SO_2$ competed for surface catalytic sites. While the former reacted with O_2 to form sulphate, the latter simply occupied the site without any further reaction. The activation energy for AC catalytic S(IV) oxidation was estimated to be $96\,\mathrm{kJ\,mol^{-1}}$, while that for deactivation by $H_2O^\bullet SO_2$ was about $21\,\mathrm{kJ\,mol^{-1}}$.

In a recent investigation, Vidal *et al.* [14] indicated that the Fe content in AC is $\leq 0.1\%$. Considering the report of Fe catalysis at $\sim 10^{-8}$ M [60, 141], 0.1% of Fe would be sufficient to promote S(IV) oxidation. Unfortunately, there has been no effort in determining how much of the AC catalysis is due to the transition metals in the AC. Neither has there been any attempt to explain how AC mechanistically interacts with S(IV) to enhance its oxidation in the presence of O_2.

6.6.2 Photochemical oxidation by excited $H_2O^\bullet SO_2$. Kerezsi *et al.* [231] recently reported a new oxidation pathway by UV-photosensitized $H_2O^\bullet SO_2$. They observed photo-induced, non-catalytic S(IV) and Fe(II) oxidation at pH < 1.0. The rate was found to be independent of O_2 and pH (pH ~ 0–1.0), but dependent of light intensity and [S(IV)]. The possibility of sensitized Fe(II) was ruled out because aqueous $H_2O^\bullet SO_2$ was much more photo-active (~5–6 orders of magnitude) than Fe(II) [55, 144, 231]. To explain the absence of $S_2O_6^{2-}$ and $S_2O_8^{2-}$ and the independence of rate on O_2, the following non-radical mechanism was proposed (equations (81)–(84)):

$$H_2O^\bullet SO_2 + h\nu(\lambda < 300\,\mathrm{nm}) \longrightarrow {}^*H_2O^\bullet SO_2 \quad [\textit{rate limiting step}] \tag{81}$$

$$^*H_2O^\bullet SO_2 + O_2 \longrightarrow HSO_5^- + H^+ \tag{82}$$

$$\mathrm{HSO_5^- + H_2O^{\bullet}SO_2 \longrightarrow 2HSO_4^- + H^+} \tag{83}$$

$$\mathrm{HSO_5^- + 2Fe^{2+} + 2H^+ \longrightarrow 2Fe^{3+} + HSO_4^- + H_2O} \tag{84}$$

This pathway was expected to be significant at pH < 1.0 with UV irradiation. Once above pH 1, the photo-assisted Fe-catalyzed pathway dominated with increasing pH.

6.6.3 $\mathbf{NO_X}$-S(IV) interactions. NO_X-S(IV) chemistry is important in atmospheric systems and applications such as flue gas desulphurization [12]. Many interactions and reactions can occur between nitrogen and sulphur oxides. They can form complexes, participate in electron transfer reactions, or form new N-S oxides [232, 233]. NO_X-S(IV) interactions are sensitive to the presence of O_2 [135], pH [12, 134, 233, 234], and metal catalysts such as Fe ions [235, 236]. Common products of NO_X-S(IV) reactions are NO_2^-, NO_3^-, SO_4^{2-}, $S_2O_6^{2-}$ [134], and N-S oxides such as $HON(SO_3)_2^{2-}$, $HONHSO_3^-$, $HN(SO_3)_2^{2-}$, $N(SO_3)_2^{2-}$ [234, 237].

NO_X-S(IV) redox reactions take place primarily at the air-water interface [12]. NO_2 accelerates the dark phase S(IV) oxidation with aerosol by about 10 times [134] via a non-catalytic radical mechanism in which the NO_2 is not regenerated [233]. Sulphate formation via N-S oxides pathway is significant only at high pH (>4) [12, 233, 234]

In the presence of Fe-L complexes, N-S interactions can proceed through co-ordination with or without Fe-L complexes, resulting in the oxidation of S(IV) and Fe(II) to S(VI) and Fe(III) [235, 236]. Both non-radical [234, 238] and radical [12, 58, 233] mechanisms have been proposed. The detailed interplay between Fe(II/III), NO_X, S(IV), intermediate N-S oxides, pH, and other organic substrates is very complicated [235, 236] and is not discussed here.

6.6.4 Surface catalyzed S(IV) oxidation. Suspensions of metal oxides such as MnO_2, V_2O_5, Al_2O_3, TiO_2 [239], Ni_2O_3, MgO [240, 241], CoO, CuO, SiO_2 [127, 242], Cu_2O [126], and Fe_2O_3 [71, 239] have been reported to catalyze S(IV) oxidation. Similar effects have also been documented for black carbon and soot [239, 243]. These oxides or particles are ubiquitous in airborne particles [30, 134], combustion residuals, and industrial systems (e.g., mineral slags).

Faust *et al.* [71] investigated Fe_2O_3-catalyzed oxidation of S(IV) in the presence of light. They proposed a mechanism in which S(IV) first became associated with a surface metal site, followed by light absorption and intra-complex electron transfer. The formation of oxidative sulphur oxyanion intermediates is dependent of the configuration of binding (mono-nuclear or bi-nuclear) and the availability of O_2. These intermediates are responsible for the oxidation of S(IV) to dithionate or sulphate. An abbreviated model proposed by Faust *et al.* [71] is shown below (equations (85)–(88)):

$$\mathrm{\|{\equiv}FeOH + HSO_3^- \longrightarrow \|{\equiv}FeOSO_2^- + H_2O} \tag{85}$$

$$\mathrm{\|{\equiv}FeOSO_2^-} + hv \longrightarrow \mathrm{\|{\equiv}FeOSO_2^{*-}} \tag{86}$$

$$\mathrm{\|{\equiv}FeOS^{IV}O_2^{*-} \longrightarrow \|{\equiv}FeOS^{V}O_2^{\bullet-}} \tag{87}$$

$$\mathrm{\|{\equiv}FeOS^{V}O_2^{\bullet-}(+O_2) \longrightarrow SO_3^{\bullet-}/SO_4^{\bullet-}/SO_5^{\bullet-}/SO_5^{2-}} \tag{88}$$

Stumm *et al.* [244] commented that the oxidation of Fe(II) could be sped up when Fe(II) became adsorbed to a surficial hydroxyl group. Thus the catalytic nature involving metal oxides may be two-fold: the surface-assisted production of oxidative intermediates and the adsorption of Fe(II).

Brodzinsky *et al.* [243] studied S(IV) oxidation under soot catalysis. They observed that S(IV) oxidation occurred faster with pre-oxygenated soot and that the activation energy of the reaction was comparable to that for O_2 chemisorption (~50 kJmol^{-1}). From these observations, they suggested that S(IV) oxidation took place when two S(IV) molecules adsorbed onto an oxygenated surface site. A similar mechanism was suggested by Prasad *et al.* [127] for SiO_2 catalysis, except that the bound S(IV) may be oxidised to $S_2^{VI}O_7^{2-}$ or $S^{VIII}O_5^{2-}$.

6.6.5 Photochemical oxidation of Fe(II) in the absence of O_2 and other reductants. In the absence of O_2 and other reductants, Fe(III) and molecular H_2 can be produced from UV-induced oxidation of Fe(II) [245]. This may be further assisted with photosensitized Fe(III) [246–248] (see sections 6.6.6 and 6.6.7). Braterman *et al.* [249] and Jortner *et al.* [246, 247] suggested the following scheme for anoxic photo-oxidation of Fe(II) (equations (89)–(95)):

$$Fe^{2+} + h\nu(\lambda < 300\,nm) \longrightarrow Fe^{2+*} \quad [pH < 3] \tag{89}$$

$$Fe^{2+*} + H_2O \longrightarrow Fe^{3+} + OH^- + H^\bullet \tag{90}$$

$$Fe^{2+*} + H^+ \longrightarrow Fe^{3+} + H^\bullet \tag{91}$$

$$Fe^{2+} + h\nu + H_2O(\lambda > 400\,nm) \longrightarrow (FeH_2O)^{2+*} \quad [pH > 6.5] \tag{92}$$

$$(FeH_2O)^{2+*} \longrightarrow FeOH^{2+} + H^\bullet \tag{93}$$

$$Fe^{2+} + H^\bullet \longrightarrow [FeH]^{\bullet 2+} \tag{94}$$

$$[FeH]^{\bullet 2+} + H^+ \longrightarrow Fe^{3+} + H_2 \tag{95}$$

6.6.6 Fe(III)-mediated photo-oxidation—radical production. Fe(III) can mediate photo-oxidation of S(IV) or organic substrates in two ways. The first is the production of radicals such as $^\bullet OH$, $SO_4^{\bullet -}$ from UV-sensitized Fe(III). The $^\bullet OH$ production from $FeOH^{2+}$ photolysis has been demonstrated in an early polymerization study [250] and recent decontamination studies [251, 252]. Photolysis of $FeOH^{2+}$/Fe(III) takes place in both UV light and sunlight [253], and is thus an importance source of radicals in atmospheric systems, surface waters, and industrial processes. The radical production reaction from photosensitized Fe(III) may be briefly summarized as follows [246, 247, 250, 254]:

$$FeOH^{2+} + h\nu \longrightarrow Fe^{2+} + {}^\bullet OH \tag{96}$$

$$(\lambda = 296[254], 313[250]\,nm)$$

$$Fe^{3+} + h\nu + H_2O \longrightarrow Fe^{2+} + {}^\bullet OH + H^+ \quad [\textit{minor pathway}] \tag{97}$$

$$(\lambda = 254\,nm, [250])$$

$$Fe^{3+} + h\nu(\lambda < 300\,nm) \longrightarrow Fe^{3+*} \tag{98}$$

$$Fe^{3+*} + (OH^-, SO_4^{2-}) \longrightarrow Fe^{2+} + ({}^\bullet OH, SO_4^{\bullet -}) \tag{99}$$

6.6.7 Fe(III)-mediated photo-oxidation—intramolecular redox reaction. Fe(III) can also facilitate photo-oxidation of reductive substrate through the formation of a stable Fe^{III}-substrate complex. This occurs only when the substrate can form a relatively stable complex with Fe(III). Upon irradiation at an appropriate wavelength, the Fe^{III}-substrate complex will absorb light and become sensitized. The complex then undergoes an intramolecular electron transfer [256]. If the substrate binds to Fe(III), it will be photo-oxidised by $^\bullet OH$ radicals produced from photo-sensitized Fe(III) [252].

The photo-oxidative path essentially depends upon the electrophilicity of the ligands coordinated to Fe(III) [255]. The ligand that is most willing to donate electron to the Fe(III) center will be oxidised. Thus electron-rich organic ligands will be preferentially oxidised, followed by anions such as SO_4^{2-} and OH^-. A generic mechanism for the Fe(III)-assisted photo-oxidation of organic molecules is expressed as the following (equations (100)–(102)) [257, 258]:

$$\mathrm{Fe^{III}\text{-}Org} + h\nu \longrightarrow (\mathrm{Fe^{III}\text{-}Org})^* \tag{100}$$

$$(\mathrm{Fe^{III}\text{-}Org})^* \longrightarrow \mathrm{Fe^{II}} + \mathrm{Org}^\bullet \tag{101}$$

$$(\mathrm{Fe^{III}\text{-}Org})^* + \mathrm{M} \longrightarrow (\mathrm{Fe^{III}\text{-}Org}) + \mathrm{M}^* \quad [\textit{thermal deactivation}] \tag{102}$$

Zuo *et al.* [258] observed the formation of H_2O_2 and the oxidation of S(IV) and dissolved organic matters in the rainwater and fogwater samples exposed to UV and visible light. The photoformation of H_2O_2 in the presence of Fe(III), O_2, and organic substrates may be expressed as equations (103)–(106) [258]:

$$\mathrm{Org}^\bullet + \mathrm{O_2} \longrightarrow \mathrm{Org}' + \mathrm{O_2^{\bullet -}} \tag{103}$$

$$\mathrm{O_2^{\bullet -}} + \mathrm{H^+} \longrightarrow \mathrm{HO_2^\bullet} \tag{104}$$

$$\mathrm{HO_2^\bullet} + \mathrm{O_2^{\bullet -}} + \mathrm{H^+} \longrightarrow \mathrm{H_2O_2} + \mathrm{O_2} \tag{105}$$

$$\mathrm{HO_2^{\bullet -}} + \mathrm{Fe(II)} + \mathrm{H^+} \longrightarrow \mathrm{H_2O_2} + \mathrm{Fe(III)} \tag{106}$$

Simple Fe(III) complexes with citrate, oxalate, malonate, pyruvate, glyoxalate [257, 258] and other uncharacterized dissolved organic carbons [42] have been reported to undergo photo-oxidation or to initiate the photoformation of H_2O_2.

6.6.8 Fenton chemistry and related systems. In the presence of Fe ions, $^\bullet OH$ can be produced from H_2O_2 (equations (107) and (108)) [218, 259].

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \longrightarrow \mathrm{Fe(III)} + {}^\bullet\mathrm{OH} + \mathrm{OH^-} \tag{107}$$

$$\mathrm{Fe(III)} + \mathrm{H_2O_2} \longrightarrow \mathrm{Fe(II)} + \mathrm{HO_2^\bullet} + \mathrm{H^+} \tag{108}$$

Kwan *et al.* [259] observed similar chemistry with Fe-oxyhydroxides (geothite, ferrihydrite, and hematite) (equations (109)–(111)).

$$\mathrm{Fe(III)} + \mathrm{H_2O_2} \longleftrightarrow \mathrm{Fe(III)H_2O_2} \tag{109}$$

$$\mathrm{Fe(III)H_2O_2} \longrightarrow \mathrm{Fe(II)} + \mathrm{HO_2^\bullet} + \mathrm{H^+} \tag{110}$$

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \longrightarrow \mathrm{Fe(III)} + {}^\bullet\mathrm{OH} + \mathrm{OH^-} \tag{111}$$

The reactivity of $^\bullet OH$ is on the same scale or may even exceed those of oxysulphur radicals (see C1 and C4 in Appendix C), and so their presence may not be neglected.

6.6.9 Fe-organo complexes catalyzed S(IV) oxidation. The S(IV) oxidation catalyzed Fe(II/III) complexes have been reported. Fe^{II}-tetrasulphphthalocyanine (Fe^{II}TSP) [77], Fe^{III}-iminodiacetate (Fe^{III}IDA), Fe^{III}-tetraethylenepentamine (Fe^{III}TH) [186], Fe^{III}EDTA [187, 188] FeIII-phenanthroline (Fe^{III}Phen) [189] were investigated. Except Fe^{III}EDTA, all were found to catalyze S(IV) oxidation, though at a rate about $\sim 10^2$ slower than the uncomplexed Fe(III) catalysis [186].

7. Critical review of current thoughts on Fe-S(IV)-O_2 chemistry

7.1 *Experimental supports for radical chain mechanism*

Studies over the past 10 to 15 years favoured the radical chain mechanism for the 'catalytic' oxidative feature in Fe-S(IV)-O_2 and other similar systems [26, 27, 60, 66], which is endorsed by several important findings.

The first was the conclusive demonstration of the existence of sulphur oxyanion radicals such as $SO_3^{\bullet-}$, $SO_4^{\bullet-}$, $SO_4^{\bullet-}$ by Hayon *et al.* [55] via high-energy photolytic analytical techniques of pulse radiolysis and flash photolysis [193, 260]. Since sulphur oxyanion radicals are the key chemical participants in the radical chain mechanism proposed by Backström, the proof of their existence also substantially validated the chain mechanism. Further radiolysis and photolysis studies were conducted by Buxton *et al.* [59, 261] to quantify the kinetics of reactions between oxysulphur radicals and other ionic, neutral, or radical species. These works demonstrated the high reactivities of $SO_X^{\bullet-}$ towards many aqueous species, including S(IV), Fe(II), and O_2, and also some relatively inert entities such as Cl^-. At the same time, various studies have shown, without the need of mechanistic speculations, that the formation of Fe(III)-S(IV) complexes (e.g., $FeSO_3^+$ and $Fe(OH)SO_3H^+$) and their subsequent decomposition determine the overall rate of induced/catalytic redox chemistry in Fe-S(IV)-O_2 system [72, 73, 114, 141, 214]. The highly reactive nature of $SO_X^{\bullet-}$ and the fact that it can be generated from the rate determining decay of Fe(III)-S(IV) species via intra-complex electron transfer coupled nicely in support for the radical chain mechanism.

A further indirect support for the chain-mechanism is the inhibition effect exhibited by organic compounds such as benzene [214], phenols [15, 161], simple alcohols [49], and terpenic derivatives [162, 176]. These organic species such as simple alcohols are well known to scavenge radicals in aqueous solutions [58, 193]. The reaction kinetics between these S(IV)-oxidation inhibitors and the key oxysulphur radicals were quantified with either radiolysis/photolysis techniques or decomposition of highly oxidative sulphur-oxide species like $S_2O_8^{2-}$ (see B7 in Appendix B for reduction potential and C4, C6 and C7 in Appendix C for specific reactions). All these findings, again, fit nicely together within the radical chain mechanism framework.

Despite the strong support for the radical mechanism in many recent studies, we have encountered concerns over the popular mechanism in the literature.

7.2 *Examination on formation of oxysulphur radicals*

7.2.1 Is formation of oxysulphur radicals energetically favourable? Oxysulphur radicals ($SO_X^{\bullet-}$, X = 3–5) are currently thought to be produced from the redox decomposition of Fe(III)-S(IV) complexes such as $FeSO_3^+$. Its production involves an intra-complex single-electron transfer from S(IV) to Fe(III). Here, we will argue that the formation of oxysulphur radicals, in particular $SO_3^{\bullet-}$ which is thought to form via the redox-decay of $FeSO_3^+$, is thermodynamically unfavourable in the absence of external energy input (e.g., the short wavelength radiation).

The oxidation of Fe(II) by pure oxygen is known to proceed slowly [81], most likely by more reactive species such as singlet oxygen ($^1O_2$). The slow rate is mainly due to the fact that the singlet oxygen concentration in an oxygenated water is low without a high-energy radiation [80]. The ΔE_H° for Fe(II) oxidation via $^3O_2$ and $^1O_2$ to Fe(III) and $O_2^{\bullet-}$ are $(-0.77 + 0.83 =)$ 0.06 V and $(-0.77 - 0.16 =)$ -0.93 V, respectively. If we consider the energy difference between the 'radical' state (i.e. Fe(III) and $O_2^{\bullet-}$) and the reactant state (i.e. Fe(III) and O_2), the $^3O_2$ path is thermodynamically unfavourable, with a $\Delta G^\circ_{rxn,3-O2}$ of 90 kJmol^{-1}—that is, the intrinsic rate of forward reaction (Fe(II)+$^3O_2 \rightarrow$ Fe(III)+$O_2^{\bullet-}$) will be much less than the rate of reverse reaction (Fe(III)+$O_2^{\bullet-} \rightarrow$ Fe(II) $+^3$ O_2).

Now, considering the ΔE°_H for the formation of Fe(II) and $SO_3^{\bullet-}$ from the redox decay of $Fe^{III}SO_3^+$ and assuming that the energy state of $Fe^{III}SO_3^+$ is not significantly different from its dissociated form (Fe(III) + SO_3^{2-}), the $\Delta E^\circ_H \cong E^\circ_H(Fe^{3+}/Fe^{2+}) + E^\circ_H(SO_3^{2-}/SO_3^{\bullet-}) = 0.77 - 1.14\,V = -0.37\,V$, implying a ΔG°_{rxn} of 36 kJ mol^{-1} > 0. Would the reduction of Fe(III) to Fe(II) be more favourable if S(IV) is oxidised to a non-radical S(V) state instead? If we approximate $E^\circ_H(S(IV)/S(V)_{\text{non-radical}})$ to be about the same as $E^\circ_H(H_2SO_3^{2-}/S_2O_6^{2-}, H^+) = -0.56\,V$, the corresponding ΔE°_H and ΔG°_{rxn} would be 0.21 V and -20 kJ mol^{-1}, respectively. Thus, given the assumptions made, it is thermodynamically more favourable for the partially oxidised S to remain in the Fe(II)-S(V) complex form, until the subsequent redox steps take place.

Although the complex is written as Fe(II)-S(V), it is very probable that, in reality, only partial electron density is transferred from S(IV) to Fe(III), resulting in a Fe(III$^{-\delta}$)-S(IV$^{+\delta}$) complex. The partial transfer of electron density within a complex has been observed and is documented for various Co(II)-complex-O_2 adducts by Tovrog *et al.* [90]. Fe(III$^{-\delta}$)-S(IV$^{+\delta}$) is thermodynamically more stable than the dissociated $SO_3^{\bullet-}$/Fe(II) form. It does not need to sustain unstable electron density (i.e., the unpaired electron on $SO_3^{\bullet-}$) but still retains the readiness to participate in further redox reactions because of the partial electron transfer.

7.2.2 Could the Fe(III) induced S(IV) auto-oxidation proceed through a complex mechanism?

Supposing the first electron transfer step ends with the formation of Fe(II)-S(V) (or more accurately Fe(III$^{-\delta}$)-S(IV$^{+\delta}$)), how may the subsequent steps proceed? What is the spontaneity for each of those steps?

Consider the following scheme:

$$\text{Fe(III)} + \text{S(IV)} \longleftrightarrow \text{Fe(III)-S(IV)} \quad [\textit{fast}] \tag{112}$$

$$\text{Fe(III)-S(IV)} \longrightarrow \text{Fe(II)-S(V)} \quad [\Delta G^\circ_b \sim -20\,\text{kJ mol}^{-1}] \tag{113}$$

$$\text{Fe(II)-S(V)} +^3 O_2 \longrightarrow \text{Fe(II)-S(VI)} + O_2^{\bullet-} \quad [\Delta G^\circ_c \sim -6\,\text{kJ mol}^{-1}]^* \tag{114}$$

$$^*E^\circ_H(S(V)_{\text{non-radical}}/S(VI)) \sim E^\circ_H(S_2O_6^{2-}/SO_4^{2-}, H^+ = 0.22\,V), \quad \text{see B7.}$$

The fate of resulting $O_2^{\bullet-}$ may be coupled with the regeneration of Fe(III):

$$O_2^{\bullet-} + H^+ \longrightarrow HO_2^\bullet \quad [\textit{fast}]^{**} \tag{115}$$

$$^{**}\text{At } pK_a(HO_2^\bullet) = 4.8[259], \quad \text{thus at pH} < 4,\ HO_2^\bullet \ \text{ is the predominant form}$$

$$\text{Fe(II)-S(VI)} \longrightarrow \text{Fe(II)} + \text{S(VI)} \quad [\textit{fast}] \tag{116}$$

$$\text{Fe(II)} + HO_2^\bullet \longrightarrow \text{Fe(III)} + HO_2^- \quad [\Delta G^\circ_c \sim +2\,\text{kJ mol}^{-1}] \tag{117}$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \quad [\textit{fast}] \tag{118}$$

H_2O_2 is capable of reducing Fe(III) back to Fe(II), but the intrinsic rate for this reaction is much inferior to the oxidation of Fe(II) by $HO_2^\bullet$ or by H_2O_2:

$$\text{Fe(II)} + HO_2^\bullet(+H^+) \longrightarrow \text{Fe(III)} + H_2O_2 \quad [k = 1.2 \times 10^6\,M^{-1}\,s^{-1}]^{[262]} \tag{119}$$

$$\text{Fe(II)} + H_2O_2(+H^+) \longrightarrow \text{Fe(III)} + H_2O_2 \quad [k \sim 60\,M^{-1}\,s^{-1}]^{[263,264,265]} \tag{120}$$

$$\text{Fe(III)} + H_2O_2 \longrightarrow \text{Fe(II)} + HO_2^\bullet + H^+ \quad [k = 2 \times 10^{-3}\,M^{-1}\,s^{-1}]^{[266,267]} \tag{121}$$

$$\text{Fe(III)} + H_2O_2 \longrightarrow \text{Fe(II)} + {}^\bullet OH + OH^- \quad [k = 76\,M^{-1}\,s^{-1}]^{[218]} \tag{122}$$

The proposed scheme can explain the key features of Fe-S(IV) induced redox chemistry. It can explain the stepwise oxidation of S(IV) and the regeneration of Fe(III) by O_2, the ultimate electron acceptor. With the presence of $O_2^{\bullet -}$, it can explain the inhibiting effect of organic molecules on the Fe-catalyzed S(IV) oxidation.

7.2.3 Would the formation of S-O_2 and Fe-O_2 adducts be possible? Could an O_2 adduct be formed with an Fe(II)-S(V) complex via a O-S linkage?. $SO_3^{\bullet -}$ reacts readily with O_2 to form $SO_5^{\bullet -}$. This reaction is both thermodynamically and kinetically favoured ($\Delta G^\circ_{rxn} = \Delta G^\circ_f\,(SO_5^{\bullet -}) - \Delta G^\circ_f\,(SO_3^{\bullet -}) - \Delta G^\circ_f\,(O_2) \sim -490 - (-426) = -64\,\text{kJ mol}^{-1}$; $k_f = 1.1 - 2.5 \times 10^9\,M^{-1}\,s^{-1}$) (see B9 in Appendix B and C2 in Appendix C). Supposing the additional stability of complexed S(V) over radical S(V) is about the same as the ΔE°_H between the $E^\circ_H(S(IV)/S(V)_{\text{non-radical}})$ and E°_H $(SO_3^{2-}/SO_3^{\bullet -})$ couples, the $\Delta G^\circ_f(S(V)_{\text{non-radical}}) \sim \Delta G^\circ_f(SO_3^{\bullet -}) - nF|\Delta E^\circ_H|/1000 = -426 - F(1.14 - 0.56)/1000 = -426 - 56 \cong -480\,\text{kJ mol}^{-1}$ (if estimated as 1/2 of $\Delta G^\circ_f(S_2O_6^{2-})$ $(-1004\,\text{kJ mol}^{-1})$, $\Delta G^\circ_f(S(V)_{\text{non-radical}}) = -502\,\text{kJ mol}^{-1}$.). Both estimates of $\Delta G^\circ_f(S(V)_{\text{non-radical}})$ (-480 to $-500\,\text{kJ mol}^{-1}$) are in the vicinity of $\Delta G^\circ_f(SO_5^{\bullet -})$ $(-490\,\text{kJ mol}^{-1})$, and so the formation of a SO_X-peroxo adduct by Fe(II) is thermodynamically possible, i.e.:

$$\text{Fe(II)-S(V)} + O_2 \longrightarrow \text{Fe(II)-(S(V)-O-O}^\bullet) \qquad (123)$$

The remaining structure in the complex may partially stabilize the peroxo-functionality, and should be less reactive than $SO_5^{\bullet -}$. Following reactions may take place in a manner analogous to those with $SO_5^{\bullet -}$:

$$\text{Fe(II)-(S(V)-}O_2^\bullet) + \text{Fe(II)} \longrightarrow \text{Fe(II)-(S(V)-}O_2^-) + \text{Fe(III)} \qquad (124)$$

$$\text{Fe(II)-(S(V)-}O_2^\bullet) + \text{S(IV)} \longrightarrow \text{Fe(II)} + 2\text{S(VI)} \qquad (125)$$

A similar peroxo- adduct may be formed between Fe(III) and O_2 via an Fe-O linkage, i.e. $^\bullet O_2$-Fe(III)-S(IV), as suggested in Boyce *et al.* [77].

7.2.4 When would oxysulphur radicals be important? Radiolysis, photolysis, and induced $S_2O_8^{2-}$ decomposition studies have demonstrated the existence of oxysulphur radicals. Although explicit, direct evidence of oxysulphur radicals in the Fe-S(IV)-O_2 system has been lacking, their existence in the system has often been claimed. There are studies (e.g., [36, 37]) that have quoted the $SO_X^{\bullet -}$ radical chain mechanism as the valid model, or even proposed a chain mechanism that catered to their specific cases, without providing any direct or indirect evidence.

Studies that have demonstrated the presence of $SO_X^{\bullet -}$ often involves the input of external energy such as UV-vis radiation, addition of highly reactive oxidants such as $S_2O_8^{2-}$, or employment of catalytic systems working in a combination with oxidative species. The following is a brief summary on when oxysulphur anion radicals have been explicitly observed. With this list, we hope to question the claim about the existence of $SO_X^{\bullet -}$ and HSO_5^-/SO_5^{2-} (produced from $SO_X^{\bullet -}$-O_2 reactions) in the Fe-S(IV)-O_2 systems under ‘ordinary’ conditions (i.e., no irradiation or sustantial heating, no initial presence of highly oxidative species.).

Pulse radiolysis and flash photolysis techniques are two of the most common techniques to generate oxysulphur radicals [53–55, 57, 58, 185, 197, 198, 260, 268–272]. Essentially, both techniques bombard an aqueous solution with short wavelength (<300 nm) to induce the formation of radicals. For example, in radiolysis, μ sec-pulses of photons generated at $\sim$ 2–10 MeV [54, 55, 57] are shone onto the test solution. Following reactions then take place

[55, 268, 269, 272]:

$$H_2O + h\nu(\text{at}\,\lambda_{UV}) \longrightarrow e^-_{aq} + {}^\bullet OH + H^+ \qquad (126)$$

$$e^-_{aq} + N_2O + H^+ \longrightarrow N_2 + {}^\bullet OH \qquad (127)$$

$$^\bullet OH + SO_X^{2-} \longrightarrow SO_X^{\bullet -} + OH^- \quad [X\text{: }2\text{–}4] \qquad (128)$$

The presence of these radicals was affirmed by absorbance measurement at their characteristic wavelengths.

Sun *et al.* [273] documented the enzymatic production of $SO_3^{\bullet -}$ by xanthine oxidase, a human liver enzyme, in the presence of H_2O_2. The enzymatic action reduced the activation barrier toward S(V) radical formation, while the oxidative $H_2O_2(E^\circ_H(H_2O_2, H^+/H_2O) = 1.77\,V)$ drived the production of $SO_3^{\bullet -}$ from S(IV). It was uncertain if $SO_3^{\bullet -}$ was generated in the xanthine oxidase-O_2 combination.

Gilbert *et al.* [201] reported the production of $SO_4^{\bullet -}$ from $S_2O_8^{2-}$ induced by transition metal ions such as Cu^I, Fe^{II}, Ti^{III} (equation (129)), or from Ti^{III}/Fe^{II}-(EDTA/NTA/DTPA) complexes in the presence of HSO_5^- (equation (130)).

$$Fe^{2+}/Cu^+/Ti^{3+} + S_2O_8^{2-} \longrightarrow Fe^{3+}/Cu^{2+}/Ti^{4+} + SO_4^{\bullet -} + SO_4^{2-} \qquad (129)$$

$$Fe^{II}L + HSO_5^- \longrightarrow Fe^{II}L + SO_4^{\bullet -} + OH^- \qquad (130)$$

$$(\text{where } L = \text{EDTA, NTA, DTPA})$$

Fischer *et al.* [144] reported $SO_3^{\bullet -}$ formation from HSO_3^-/SO_3^{2-} photodecomposition ($\lambda > 200\,nm$) in the absence of O_2 and the eventual formation of sulphate and $S_2O_6^{2-}$. The $S_2O_6^{2-}$ was formed via $SO_3^{\bullet -}$ recombination; sulphate formation in the absence of oxygen was left unexplained. However, sulphate was reported to be produced ‘at the expense of dithionate’. This, together with the reaction between $H^\bullet$ and $S_2O_6^{2-}$ allows us to speculate on the following mechanism for sulphate production:

$$SO_3^{\bullet -} + H_2O \longrightarrow HSO_4^- + H^\bullet \qquad (131)$$

In the presence of O_2, the formation of $S_2O_8^{2-}$ via the recombination reaction of $SO_5^{\bullet -}$ was reported.

The sulphate ion radical, $SO_4^{\bullet -}$, can be generated from $S_2O_8^{2-}$ ($E^\circ_H(S_2O_8^{2-}/SO_4^{2-}) = 2.0\,V$) by photolysis (photoactivation), chemical activation, or thermolysis (thermal decomposition) [274]. Examples of $SO_4^{\bullet -}$ production from photolysis ($\lambda = 248\,nm$ [275], 351 nm [199]) of $S_2O_8^{2-}$ can be found [193, 199, 275, 276]. Transition metal ions such as Au, Co, Cu, Fe, Mn are also known to induce decomposition of $S_2O_8^{2-}$ to $SO_4^{\bullet -}$ [274] and refs. within, [277]. The rate of activation can be further enhanced when a relatively reducing oxysulphur anion is present [277] or when the metal ion is chelated [278]. Sulphate ions generated from $S_2O_8^{2-}$ is highly temperature dependent [178, 274] (see also C7 in Appendix C).

Deister *et al.* [38] investigated the photo-oxidation of sulphite/bisulphite at $\lambda = 254\,nm$ and claimed the presence of oxysulphur radicals from the inhibitive effect of alcohols on S(IV) oxidation.

Ozawa *et al.* [225] independently found a chemically-induced pathway for $SO_3^{\bullet -}$ generation. They were able to generate $SO_3^{\bullet -}$ from S(IV) at pH 2.5 in the presence of oxidative Ce^{4+} ($E^\circ_H(Ce^{4+}/Ce^{3+}) = 1.72\,V$) (see also ΔE°_H for the $SO_3^{\bullet -}$ formation from SO_3^{2-} and Ce^{4+} in table B10 in Appendix B) and at pH 9 in the presence of $Ti^{III}EDTA$-H_2O_2. The presence of the sulphite radical was ascertained by its electron spin resonance signal.

From the above list, it is doubtful that $SO_X^{\bullet -}$ radicals can be formed solely from the catalytic action of Fe(III) without radiation or other powerful oxidants (e.g., H_2O_2, $S_2O_8^{2-}$) which have an $E^{\circ}_{H,red}$ exceeding that of O_2/H_2O couple. In the case of Ce^{4+}, its oxidizing power is comparable with that of H_2O_2/H_2O couple. Hence, one may argue about the importance of oxysulphur radicals in atmospheric systems where high-energy radiation and powerful oxidants are plentiful. However, their roles in the ordinary dark Fe-catalysis of S(IV) (or other reductants) oxidation deserve to be questioned and should be further investigated.

7.3 *Examination on the inhibition of Fe induced S(IV) auto-oxidation*

7.3.1 Are auto-oxidation 'inhibitors' simply reductants? Another piece of evidence that supports the radical chain model is the observed inhibition of S(IV) oxidation (section 5.4; also [26, 66] and refs. within) by those often referred as radical scavengers.

Studies have shown these chemical classes inhibiting catalytic S(IV) oxidation to various extents, but their reductive nature is often ignored during data analysis. Rudzinski [178] studied the effect of isoprene on S(IV) oxidation induced by Mn(II). It was observed that the induction period became longer with a higher level of isoprene. A similar observation was also made by Wolf *et al.* [182] when oxalate was present in an Fe-S(IV)-O_2 system. A prolonged induction period is also observed when the system has relatively high initial [Fe(II)]/[Fe(III)], [S(IV)]/[Fe(III)], or SO_2/O_2 ratios (see sections 5.1.1 and 5.2.4). Kulkarni *et al.* [15] have shown a complete degradation of phenol in a Cu-S(IV)-O_2 system. Thus, the inhibitive effect of these organic inhibitors may be simply due to their reductive nature, rather than their particular radical-scavenging properties.

The fact that inhibitors react with $SO_X^{\bullet -}$ radicals readily (see C9 in Appendix C) does not necessarily lead to the same radical pathway involved in the Fe-S(IV)-O_2 redox chemistry. Given the observation of slower S(IV) oxidation and prolonged induction period (e.g. [49, 178, 179]) one may only claim that Fe(III) and S(IV) together induce dissolved O_2 to some activated form that can undergo electron transfer reaction readily. Reductants, such as S(IV), organic reductants, and perhaps also reduced metals, will compete with each other to react with the activated form of O_2. Essentially, Fe(III)-S(IV) interaction serves as a catalytic shuttle for electron transfer between O_2 and aqueous reductants.

The extent of inhibitive effect will depend primarily on the relative abundance of inhibitors to S(IV), and the relative reactivities between the reductants with O_2 in the redox-activated form. Thus, even when the inhibitive effect is 'significant' and [S(IV)] $\gg$ [inhibitors], it may not be concluded that the inhibitive effect is due to the radical quenching, since the possibility of the organic molecules being more reactive reductants than S(IV) exists.

It is rather misleading to call chemical species such as alcohols, phenols, and benzenes as 'inhibitors', if they do not deactivate the metal catalyst by complexation, but simply compete with S(IV) as reductants in the metal-catalyzed S(IV)-O_2 system. Ziajka *et al.* [49, 179] studied the effects of terpenic alcohols on S(IV) auto-oxidation under Fe(III) catalysis, and showed that for alcohols and some terpenic derivatives, the inverse of S(IV) oxidation rate was proportional to the amount of competing reductant added. This suggests the decay of terpenic derivatives increases as the rate of S(IV) oxidation decreases. Similar results were also found in [178]. Pasiuk-Bronikowska *et al.* [162] further showed that phenolic species also competed with S(IV) oxidation in non-catalytic system.

7.3.2 Can the diminished S(IV) oxidation rate be explained without radical scavengers? Ziajka *et al.* [49, 179] brought the classical expression on auto-oxidation inhibition kinetics by Alyea *et al.* [1] into the context of a radical chain mechanism, and successfully fitted most of their experimental data. They first formulated a chain termination rate as a sum of two terms (equation (132)), and then showed, after making some assumptions, that the inverse of S(IV) oxidation rate can be related to the concentration of the inhibitor (here alcohol, 'alc') (equation (133)):

$$r_{\mathrm{term}} = k_1[\mathrm{Fe(II)}][\mathrm{SO}_5^{\bullet-}] + k_2[\mathrm{alc}][\mathrm{SO}_4^{\bullet-}] \tag{132}$$

$$\left\{\frac{d[\mathrm{S(IV)}]}{dt}\right\}^{-1} = \frac{A + B[\mathrm{S(IV)}]}{[\mathrm{alc}]} \tag{133}$$

where [Fe(II)] and other rate constants condense into A and B. An equation of the same form as (equation (133)) can be obtained if other oxidative intermediates (e.g., $^{\bullet}$OH, $O_2^{\bullet-}$, or oxygenated complexes, etc) are used instead of $SO_4^{\bullet-}$ and $SO_5^{\bullet-}$. The experimental data may be explained equally well by other oxidative intermediates, and hence a non-oxysulphur radicals chain mechanism may be equally valid.

7.3.3 Other remarks on inhibitive effects. Inhibitor studies can be conclusive of the catalytic S(IV) auto-oxidation involving oxysulphur radicals only when the products are strictly due to the presence of oxysulphur radicals and nothing else. While many studies had shown the inhibiting effect of organic compounds and radical scavengers on Fe(II) oxidation or S(IV) oxidation, they rarely characterize the reaction pathway or the end-products of the reactions. [49, 162, 176, 178, 179]. Two particular studies will be commented in this respect as examples.

Kharchenko *et al.* [6] studied CN^- oxidation in Cu(II)-S(IV)-O_2. They tested for the involvement of radical species with acrylonitrile. It was found that polymerization did not occur when CN^- was in contact with S(IV)-O_2 only, but acrylonitrile polymerized when Cu(II) was added. The finding was attributed to the formation of $SO_3^{\bullet-}$ from Cu(II)-S(IV) electron transfer, with the key oxidation step of CN^- proposed to be a three-electron transfer step:

$$\mathrm{SO}_5^{\bullet-} + \mathrm{CN}^- \longrightarrow \mathrm{SO}_4^{2-} + \mathrm{CNO}^{\bullet} \tag{134}$$

But is this reaction thermodynamically favourable? $E_H^o(\mathrm{CNO}^{\bullet}/\mathrm{CNO}^-) = 2.66\,\mathrm{V}$ [279], and $E_H^o(\mathrm{CNO}^-, \mathrm{H_2O}/\mathrm{CN}^-, \mathrm{OH}^-) = 0.97\,\mathrm{V}$ (i.e. (equation (135)), [280]), which gives: $E_H^o(\mathrm{CNO}^{\bullet}/\mathrm{CN}^-) = 3.63\,\mathrm{V}$ (equations (136) and (137)).

$$\mathrm{CNO}^- + \mathrm{H_2O} + 2e^- \longrightarrow \mathrm{CN}^- + 2\mathrm{OH}^- \quad [E_H^o = 0.97\,\mathrm{V}] \tag{135}$$

$$\mathrm{CNO}^{\bullet} + e^- \longrightarrow \mathrm{CNO}^- \quad [E_H^o = 2.66\,\mathrm{V}] \tag{136}$$

$$\mathrm{CNO}^{\bullet} + 3e^- + \mathrm{H_2O} \longrightarrow \mathrm{CN}^- + 2\mathrm{OH}^- \quad [E_H^o = 3.63\,\mathrm{V}] \tag{137}$$

Taking the highest $E_H^o(\mathrm{SO}_5^{\bullet-}/\mathrm{SO}_5^{2-}) \leq 1.4\,\mathrm{V}$ [57] (equation (138)) and $E_H^o(\mathrm{SO}_5^{2-}/\mathrm{SO}_4^{2-}) \sim 1.8\,\mathrm{V}$ (from table B7 in Appendix B) (equation (139)) gives an $E_H^o(\mathrm{SO}_5^{\bullet-}/\mathrm{SO}_4^{2-}) \sim 3.2\,\mathrm{V}$ (equation (140)).

$$\mathrm{SO}_5^{\bullet-} + e^- \longrightarrow \mathrm{SO}_5^{2-} \quad [E_H^o \leq 1.4\,\mathrm{V}] \tag{138}$$

$$\mathrm{SO}_5^{2-} + 2e^- + 2\mathrm{H}^+ \longrightarrow \mathrm{SO}_4^{2-} + \mathrm{H_2O} \quad [E_H^o \sim 1.8\,\mathrm{V}] \tag{139}$$

$$\mathrm{SO}_5^{\bullet-} + 3e^- + 2\mathrm{H}^+ \longrightarrow \mathrm{SO}_4^{2-} + \mathrm{H_2O} \quad [E_H^o \sim 3.2\,\mathrm{V}] \tag{140}$$

This would give a ΔE_H^o for reaction (**7.6**) $\sim 3.2\,\mathrm{V}–3.6\,\mathrm{V} = -0.4\,\mathrm{V}$, implying the reaction is not spontaneous. Furthermore, Kharchenko *et al.* [6] commented that CN^- is well known to reduce free, uncomplexed Cu(II) to produce $CN^{\bullet}$ radical (equation (141)), which may dimerize (equation (142)) or further react to form CNO^- (equation (143)).

$$Cu^{2+} + CN^- \longrightarrow Cu^+ + CN^{\bullet} \tag{141}$$

$$2CN^{\bullet} \longrightarrow (CN)_2 \tag{142}$$

$$(CN)_2 + 2OH^- \longrightarrow CNO^- + CN^- + H_2O[280] \tag{143}$$

Their data showed that in the absence of Cu(II), CN^- decayed in the Na_2SO_3-$Na_2S_2O_5$ exposed to atmospheric O_2, noting that $S_2O_5^{2-}$ decomposes to give S(IV). Without characterizing the end-products of CN^- oxidation, the fate of S(IV) or Cu(II), and even the temperature, it is not clear what had caused the polymerization of acrylonitrile.

The work of Pasiuk-Bronikowska *et al.* [48] gave a stronger evidence for the involvement of oxysulphur radicals in the Fe(III)-S(IV)-O_2 system. They investigated toluene, naphthalene, paraffin oil sulphonation in the Fe(III)/Mn(II)/Co(II)-S(IV)-O_2 systems. Their HPLC analysis demonstrated the formation of sulphonated toluenes and naphthalenes over time, which, they concluded, were formed from the recombination of organo-radical and $SO_3^{\bullet-}$ radical.

Their proposed reaction is not consistent with the classical $SO_X^{\bullet-}$ chain model. In the classical model, $SO_3^{\bullet-}$ preferentially combines with O_2 to form the highly oxidative $SO_5^{\bullet-}$, which is the key chain-branching radical [66]. The formation of $SO_5^{\bullet-}$ from $SO_3^{\bullet-}$ and O_2 is also spontaneous ($\Delta G^o_{rxn} \sim -60\,kJmol^{-1}$, from B9 in Appendix B). Thus it is unlikely to have free floating $SO_3^{\bullet-}$ radicals encountering an aromatic radical, as $SO_3^{\bullet-}$ radicals are much less available than O_2. Given that their experiments were conducted at temperature ranging from 53 to 90 °C, the sulphonated organics observed likely come from the direct sulphonation reaction between S(IV) and the aromatics. The sulphonation of aromatic compounds is rather well documented [281], and the removal of water or heating are known to promote sulphonation. Unfortunately, no control experiments were reported for a background sulphonation signal from a S(IV)-organic substrate-only system [48]. In addition, the timescale of the reaction (4–8 hrs) sharply contrasts the typical lifetime of the Fe-S(IV)-O_2-inhibitors reaction, 5–20 mins as in [178, 49].

Although the oxidation of benzene to phenol has been demonstrated in the Fe-S(IV)-O_2 system by Deister *et al.* [38] and Travina *et al.* [163], the results were not conclusive on the involvement of oxysulphur radicals because photolysis and powerful oxidants were used (see section 7.2.4).

Not all reported inhibition effects are attributed to radical scavenging. For instance, Krause [74] reported an inhibition effect by thiourea (H_2NCSNH_2) and thiocyanide (SCN^-). Having a similar structure as aldehydes, thiourea may form an adduct with S(IV); thiocyanide, on the other hand, probably inactivates the Fe center via complexation. The report of possible interference of O_2 on the radical-scavenging of hydroquinone [150] also cast doubts on the oxysulphur radical pathway being the only viable model for the catalytic S(IV) or Fe(II) oxidation.

8. Discrepancies and difficulties

8.1 *Disagreement and discrepancies*

8.1.1 Nature of non-catalytic S(IV) oxidation. There seem contrasting views on the existence of uncatalyzed S(IV) oxidation, mainly due to the fact that the contamination by trace metal ions is difficult to eliminate [43, 132]. Studies showed that as little as $\sim 10^{-8}$ M of

Fe(III) is sufficient to initiate S(IV) oxidation [51, 282] and small quantities of strong chelating agents such as EDTA and phenanthroline could also stop the reaction [76, 116, 185, 189]. Ermakov and Purmal [60] pointed out that the residual $[\text{Fe}]_{\text{Tot}}$ in typical deionized waters was about $2\text{–}50 \times 10^{-8}$ M and the estimated trace Fe in typical non-catalytic studies ranged from $3\text{–}20 \times 10^{-9}$ M. Based on these estimates and the fact that the trace contamination is hard to avoid, they suggested that there was no truly non-catalytic S(IV) oxidation. The S(IV) oxidation observed in all cases was suggested to be due to trace Fe ions present in the system. They even argued that the reported catalysis by other transition metal ions in low valence states (e.g., Mn(II), Fe(II)) was all initiated by trace Fe(III) in the system.

The potential importance of trace metal was not accepted or recognized by others [38, 114, 121, 144, 156]. In fact, very few non-catalytic studies have taken sufficient precautions against trace metal contamination: reactors in most studies were made of glass rather than teflon [98]; solutions were predominantly prepared from deionized water rather than double- or triple-distillated water. Other sources of uncertainty are inadequate cleaning procedure, not using gaseous SO_2 as the S(IV) source and impurities in stock chemicals such as buffering agents or concentrated acid.

8.1.2 Reaction order and its dependence of reactants. A great variation in the reaction order and its dependence of individual reactants has been reported for the Fe-S(IV)-O_2 and similar systems [26, 77, 112, 160]. Some of the reported inconsistency, for example the varying order dependence upon [S(IV)] and $[O_2]$ in packed column studies, is probably due to specific reactant(s) being limiting. For systems involving gases, the limiting effect due to slow mass transfer can also be important [229, 230]. For instance, Brandt *et al.* [94] observed that the rate of S(IV) auto-oxidation had an O_2 dependence at pH 2.5 but not at pH 6.1. This can be explained from the general trend that S(IV) oxidation rate declines dramatically as pH moves away from the optimal range of $\sim$3 to 5 (section 5.2.5). Others gave mixed-order rate expressions (e.g., [98, 127, 160, 283]) that may be empirically useful but have vague kinetic meanings. In the studies where O_2 is not limiting, the disagreement on the reaction order for [S(IV)] and [Fe(II/III)] also exists: some proposed a 1.5 order dependence on [S(IV)] and 0.5 order on [Fe], while first-order dependence for both [S(IV)] and [Fe] was adopted in other studies [26, 77, 112]. The reaction order of $[H^+]$ also varies greatly [26, 141]. While a part of the inconsistency may be attributed to different mechanistic interpretations in literature (i.e. radical vs complex mechanism) [112, 208], a substantial portion of the disagreement seems rooted in the ignored role of [S(IV)] and [Fe] speciation. For instance, the explicit $[H^+]$ dependence should disappear if individual S(IV) or Fe(III) species are expressed. Only very few studies (e.g., [136]) considered speciation in the kinetic analysis. Furthermore, different forms of Fe(III) and S(IV) behave differently in complexation or redox reactions (B3, B5, C1, etc in the Appendices). Unfortunately, a fundamental concept as such has slipped away from numerous redox kinetic studies on the Fe-S(IV)-O_2 system.

8.1.3 Catalysis by transition metals at low valence states (Fe(II), Mn(II), etc). A number of studies have reported S(IV) auto-oxidation catalyzed by low-valence transition metals, such as Fe(II), Mn(II), and Cu(II) [13, 50, 64, 98, 132, 178]. Co(II) and Pb(II) were found to increase S(IV) oxidation rate at pH > 6 [50, 64]. Cr(III), V(IV), and V(V) were reported to have little catalytic activity over the autoxidation of S(IV) [77, 94, 123, 284, 285]. Dasgupta *et al.* [131], however, reported no catalytic effect by Mn(II), Co(II), Ni(II), and As(III).

Ermakov and Purmal [141] showed that production $SO_3^{\bullet-}$ from S(IV) with Mn(II) as electron acceptor is thermodynamically unfavourable (see B10 in Appendix B) and claimed that the ubiquitous Fe(III) were the true catalysts for 'Mn(II) catalysis' and catalysis due to other low valence transition metal ions. In the case of Mn(II) catalysis, they claimed, oxidative intermediates (e.g. $SO_X^{\bullet -}$) formed from Fe(III) catalysis initiated the formation of Mn(III), which was catalytically more effective than Fe(III) itself. This seems to support an observation by Huss *et al.* [150] in which a long induction period was found in the presence of Fe(II) but not Mn(II). The claim of Mn(III) being a better catalyst than Fe(III) is also supported by the measured intrinsic rates ($\mathrm{Mn(III)} + \mathrm{S(IV)} \rightarrow SO_3^{\bullet -} + \mathrm{Mn(II)}$, $k \sim 10^6\,\mathrm{M^{-1}\,s^{-1}}$; $\mathrm{Fe(III)} + \mathrm{S(IV)} \rightarrow SO_3^{\bullet -} + \mathrm{Fe(II)}$, $k \sim 10^{-1}\,\mathrm{M^{-1}\,s^{-1}}$). Boyce *et al.* [77] studied the S(IV) auto-oxidation with Co(II), Fe(II), Mn(II), Cu(II), Ni(II), and V(IV), chelated by tetrasulphphthalocyanine (TSP). They found that S(IV) oxidation proceeded considerably in the case of Co(II)-TSP, followed by Fe(II)-TSP, and Mn(II)-TSP, and no catalytic effect was observed with the complexes of Cu(II), Ni(II), and V(IV).

As a final note, if Ermakov and Purmal's denial of Mn(II)-$SO_3^{\bullet -}$ catalysis based on an energetic argument is appropriate, then the Fe(III)-$SO_3^{\bullet -}$ catalytic pathway, a view which they themselves and many others have firmly endorsed, should likewise be unfavourable (see B10 in Appendix B) in the absence of UV light or powerful oxidants.

8.2 *Experimental difficulties*

8.2.1 Determining intrinsic rates for radical reactions. Determining intrinsic rates for reactions involving oxidative oxysulphur radicals and other reactive species has been a challenge for inorganic chemists. Rate constants determined by different groups for the same reaction vary substantially from each other, sometimes by orders of magnitude. For instance, the rate constant for the oxidation of HSO_3^- and SO_3^{2-} by $SO_5^{\bullet -}$ (C1, reaction C1.16 and C1.17–18 in Appendix C) varies from 10^2 to $10^8\,\mathrm{M^{-1}\,s^{-1}}$ and from 10^4 to $10^7\,\mathrm{M^{-1}\,s^{-1}}$, respectively; the rate constant for the oxidation of HSO_3^- by HSO_5^- to $2HSO_4^-$ ranges from 10^2 to $10^5\,\mathrm{M^{-1}\,s^{-1}}$ (reaction C1.21 in C1 in Appendix C). Das [54] has also highlighted this problem for specific reactions. The orders of magnitude discrepancies in intrinsic rates for key reactions will reduce the credibility of insights derived from pure kinetic analyses, such as those performed in [60, 66, 141].

Oxysulphur radicals reactions are often studied using pulse radiolysis or flash photolysis techniques. Corrections for background reactions are needed, though they are not often performed. For example, following side reactions can take place while generating the desired sulphur oxyanion radicals [54, 185, 271, 272] (equations (144)–(147)):

$$e^-_{(aq)} + N_2O \longrightarrow {}^{\bullet}O^- + N_2 \quad [k = 9.1 \times 10^9\,\mathrm{M^{-1}\,s^{-1}}] \tag{144}$$

$$e^-_{(aq)} + O_2 \longrightarrow O_2^{\bullet -} \quad [k = 1.9 \times 10^{10}\,\mathrm{M^{-1}\,s^{-1}}] \tag{145}$$

$${}^{\bullet}O^- + H_2O \longrightarrow {}^{\bullet}OH + OH^- \quad [k = 9.4 \times 10^7\,\mathrm{M^{-1}\,s^{-1}}] \tag{146}$$

$${}^{\bullet}O^- + O_2 \longrightarrow O_3^{\bullet -} \quad [k = 2.0 \times 10^9\,\mathrm{M^{-1}\,s^{-1}}] \tag{147}$$

There are also other reactive radicals or species, e.g., ${}^{\bullet}H$, $HO_2^{\bullet}$, H_2O_2. Effects due to these reactive species are not insufficiently accounted for in early pulse radiolytic or flash photolytic literature.

8.2.2 Experimental artifacts due to mass transfer limitation. Both the oxysulphur radical mechanism and the complex-mediated model suggest that the formation of Fe(III)-S(IV) and its subsequent single electron transfer be the rate limiting step in the entire redox reaction network in aqueous Fe-S(IV)-O$_2$ system. O$_2$ is unlikely a limiting factor on the overall rate when it is relatively abundant compared with Fe or S(IV). Hence the rate expression should have no O_2 dependence. However, mass transfer limitation can be problematic in particular for Fe-$SO_{2(g)}$-$O_{2(g)}$ systems. For instance, Tiwari *et al.* [4] found that the rate of Fe(II) oxidation in their system increased with mixing speed, and thus their kinetic data could not be used to establish a reliable rate expression unless interfacial mass transfer parameters were known. This also weakened their subsequent claims on the equilibrium meaning of $[Fe^{3+}]/[Fe^{2+}]$ ratio and sulphate selectivity. Similarly, the studies by Ferron *et al.* [115] and Zhang *et al.* [39] were likely conducted under O_2-limiting conditions considering their elevated temperatures and the speed of auto-oxidation. Only very few studies have experimentally verified and eliminated O_2-limiting conditions (e.g., [74]). Additional considerations and mass exchange performances have to be dealt with [229, 230]. All these bring in extra interpretational difficulties, for example, in kinetic data analysis or the mechanistic role of O_2.

8.2.3 Buffer interference. There is a potential interference on S(IV) auto-oxidation from buffering agents. Drexler *et al.* [286] investigated S(IV) oxidation by peroxo-species in an acidic regime and obtained a rate expression that depended on the buffer type (chloroacetic acid, formic acid, acetic acid, and $H_2PO_4^-$) and concentration. Ramdon *et al.* [287] observed that Cr(VI)-catalyzed S(IV) oxidation increased with the concentrations of phosphate and citrate in an acidic range. Van Dyke *et al.* [288] also documented that buffers such as Tris, carbonate, HEPES, MES, MOPS could interfere with the redox system involving radicals. They commented that phosphate was the most inert towards $^{\bullet}OH$. Unfortunately, phosphate is likely to suppress the catalytic activity of Fe(III) via complex formation (log β for $Fe^{III}HPO_4^+$ and $Fe^{III}H_2PO_4^{2+} \sim 24$, comparable to that of Fe^{III}EDTA or Fe^{III}HEDTA).

8.2.4 Miscellaneous issues. Researchers in the field are facing several other challenges. One is the interpretation of absorption spectra of the Fe-S(IV)-O_2 system. Earlier researchers [43, 73, 94, 114, 136] examined absorption spectra of Fe-S(IV) solution to study kinetics of Fe-S(IV) interactions. However, these studies did not quantitatively distinguish the contributions from various Fe complexes to the spectra. More recently, Lente *et al.* [45] adopted a more vigorous approach towards the problem. The number of light absorbing species and their relative contribution at specific emission wavelengths were determined by performing matrix rank analysis on the time-resolved spectra.

Several studies have attempted to understand the redox chemistry in the Fe-S(IV)-O_2 system via 'similar' systems. They started with Fe(III), O_2, and powerful oxysulphur oxidants such as HSO_5^- and $S_2O_8^{2-}$, and tried to extend the observations from these systems to Fe-S(IV)-O_2 [163, 216]. These systems are substantially different from the Fe-S(IV)-O_2 system because both HSO_5^- and $S_2O_8^{2-}$ are much more oxidative than O_2 (see B7, B8 in Appendix B). The complicated chemistry of $S_2O_8^{2-}$ has been partly mentioned in section 7.2.4. It should also be mentioned that under an acidic condition, which is the typical setting for Fe catalytic S(IV) oxidation studies, $S_2O_8^{2-}$ can thermally decompose in the following manner [289] (equations (148)–(150)):

$$S_2O_8^{2-} + H_2O \longrightarrow 2HSO_{4^-} + \frac{1}{2}O_2 \tag{148}$$

$$H_2S_2O_8 + H_2O(\text{acidic}) \longrightarrow H_2SO_5(\text{unstable}) + H_2SO_4 \tag{149}$$

$$H_2SO_5 + H_2O(\text{acidic}) \longrightarrow H_2O_2 + H_2SO_4 \tag{150}$$

Early in the 1920's, Mathews *et al.* [290] observed S(IV) auto-oxidation could be further sped up in the presence of UV light. Boyce *et al.* [77] have also shown that even room fluorescent light was sufficient to enhance the rate of S(IV) auto-oxidation. In the view that both Fe(II) and Fe(III) can get sensitized in the presence of light (section 6.6.5–7), it is crucial to separate the influence of light from the intrinsic chemical behaviour of Fe-S(IV)-O_2 system. However, many previous studies on the system have not stated clearly about the presence or the absence of light.

9. Concluding remarks and future works

Recent works have exclusively focused on obtaining rate constants for elementary reactions in the oxysulphur radical reaction network. These intrinsic rates are useful for modeling S(VI)-chemistry in atmospheric systems, but may not be applicable to industrial or engineered systems where radiation or powerful oxidants are absent. The Fe-S(IV)-O_2 system has great potential in applications such as flue gas desulphurization, decontamination, and mineral recovery. Applicational aspects of the system, such as conditions required for complete degradation of organic pollutants, are worth further investigation.

The mechanistic aspect of the Fe-S(IV)-O_2 system, in particular from the perspective of complex-mediated model, needs to be studied. The most recent works by Kraft *et al.* [43, 73] and Conklin *et al.* [44, 72, 136] only touched upon the overall behaviour in the Fe-S(IV)-O_2 system in a complex-based framework. Mechanistic details such as the intrinsic rate and/or equilibrium ratio of the intermediate steps (e.g., the formation of Fe(III)-peroxo linkage, intra-complex Fe(III) regeneration) have not been quantified.

Inhibition studies published so far have failed to document the fate of inhibitors in the Fe-S(IV)-O_2 system in an analytically satisfactory manner. There is still no direct proof for the oxysulphur radicals chain mechanism as the prevailing mechanism in the ordinary (i.e., non-radiated, unamended with powerful oxidants) Fe-S(IV)-O_2 system. More thoughtful experiments are needed to search for this proof or counter-proof.

Very few works have documented the behaviour of E_H in the Fe-S(IV)-O_2 system. The meaning of the observed hyper-E_H (>1.3 V), the reasons for its unusually long stability, its relation to specific molecules of species are still unclear. Answers to these questions will provide fundamental insights about this very interesting catalytic system.

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Appendix A: Aqueous solubilities and Henry's Law constants for selected gases

A1 *Aqueous solubilities of selected gases*

$$[O_2]_{aq} = \exp\left\{\frac{1.045\times10^6}{T^2} - \frac{5.55\times10^3}{T} + 1.88\times10^{-1}\right\} \qquad [T = 0\text{–}100\,°C]\ [291]$$

$$[SO_2]_{aq} = \exp\left\{\frac{-1.265\times10^6}{T^2} + \frac{1.18\times10^3}{T} - 2.49\times10^{-1}\right\} \qquad [T = 0\text{–}40\,°C]\ [291]$$

Note: T in °K, $[O_2]_{aq}$ in M $O_{2aq}/1$ atm O_2, $[SO_2]_{aq}$ in M $SO_{2aq}/1$ atm $SO_2 + H_2O$

$$X(O_{2aq}) = \exp\left\{-66.7 + \frac{87.5}{T^*} + 24.5\ln T^*\right\} \qquad [T = 0\text{–}75\,°C]\ [292]$$

$$X(SO_{2aq}) = \exp\left\{-25.3 + \frac{45.8}{T^*} + 5.69\ln T^*\right\} \qquad [T = 5\text{–}55\,°C]\ [292]$$

$$X(NO_{aq}) = \exp\left\{-62.8 + \frac{82.3}{T^*} + 22.8\ln T^*\right\} \qquad [T = 0\text{–}85\,°C]\ [292]$$

$$X(N_2O_{aq}) = \exp\left\{-60.7 + \frac{88.8}{T^*} + 21.3\ln T^*\right\} \qquad [T = 0\text{–}40\,°C]\ [292]$$

Note: T^* in T/100 (°K), $X(i_{aq})$ = mole fraction $i_{(aq)}/1$, atm $i_{(g)}$

A2 *Henry's Law constant, K_{HL}, for selected gases at 20–25 °C**

Gas	K_{HL} (bar/M)
N_2	1560[a]
O_2	790[a]
CO_2	28.8[a]
H_2S	9.8[a]
SO_2	0.81[a]
NH_3	0.017[a]
NO_2	100[b]
H_2O_2	9.5×10^{-6}[b]
O_3	106[c]

*$K_{HL,i} = P_i/[i]$.
[a]ref. [293]; [b]ref. [233]; [c]ref. [265].

Appendix B: Thermodynamic properties related to aqueous Fe-S(IV)-O$_2$ system

B1 *Acid dissociation constants for oxysulphur acids at 25 °C and $I = 0\,M$*

No.	Dissociation reactions	$pK_a = -\log K_a$	$T; I(M)$	Reference
B1.1	$^*H_2SO_3 \rightarrow HSO_3^- + H^+$	1.85	25 °C	[292]
		1.89		[291]
		1.91		[136]
B1.2	$HSO_3^- \rightarrow SO_3^{2-} + H^+$	7.18		[136]
		7.2	25 °C	[292]
		7.21		[291]
B1.3	$HSO_4^- \rightarrow SO_4^{2-} + H^+$	1.92	25 °C	[96]
		1.99	25 °C	[292, 291]
B1.4	$H_2SO_5 \rightarrow HSO_5^- + H^+$	1.0	~25 °C; I ~ 0	[57]
		1.0	25 °C	[291]
B1.5	$HSO_5^- \rightarrow SO_5^- + H^+$	9.3, 9.4	~25 °C; I ~ 0	[57, 38]
		9.86		[291]
B1.6	$H_2S_2O_3 \rightarrow HS_2O_3^- + H^+$	0.6	25 °C	[291]
B1.7	$HS_2O_3^- \rightarrow S_2O_3^{2-} + H^+$	1.74	25 °C	[291]
B1.8	$H_2S_2O_4 \rightarrow HS_2O_4^- + H^+$	0.35	25 °C	[291]
B1.9	$HS_2O_4^- \rightarrow S_2O_4^{2-} + H^+$	2.45	25 °C	[291]
B1.10	$H_2S_2O_6 \rightarrow HS_2O_6^- + H^+$	−3.4	25 °C	[291]
B1.11	$HS_2O_6^- \rightarrow S_2O_6^{2-} + H^+$	−0.2	25 °C	[291]
B1.12	$H_2S_2O_7 \rightarrow HS_2O_7^- + H^+$	−12**	25 °C	[291]
B1.13	$HS_2O_7^- \rightarrow S_2O_7^{2-} + H^+$	−8**	25 °C	[291]
B1.14	$HS_2O_8^- \rightarrow S_2O_8^{2-} + H^+$	>1.3	30–40 °C	[294]
B1.15	$NH_2SO_3H \rightarrow NH_2SO_3^- + H^+$	1.05	~25 °C	[292]
B1.16	$HON(SO_3)_2^{2-} \rightarrow ON(SO_3)_2^{3-} + H^+$	11.85	25 °C; I = 1.6	[291]
B1.17	$H_3NOSO_3 \rightarrow H_2NOSO_3^- + H^+$	1.48	25 °C; I = 1	[291]
B1.18	$Fe(SO_3)_3H_2^- \rightarrow Fe(SO_3)_3H^{2-} + H^+$	1.4	25 °C; I = 0.1	[73]
B1.19	$Fe(SO_3)_3H^{2-} \rightarrow Fe(SO_3)_3^{3-} + H^+$	2.8	25 °C; I = 0.1	[73]

$^*SO_2 + H_2O \rightarrow HSO_3^- + H^+$.
**Theoretical predicted values.

B2 *Acid dissociation constants for other acids at 25 °C and $I = 0\,M$**

No.	Dissociation reactions	$pK_a = -\log K_a$	$T; I(M)$	Reference
B2.1	$HAce \rightarrow Ace^- + H^+$	4.76		[291]
B2.2	$H_3Cit \rightarrow H_2Cit^- + H^+$	3.1		[79]
B2.3	$H_2Cit^- \rightarrow HCit^{2-} + H^+$	4.8		[79]
B2.4	$HCit^{2-} \rightarrow Cit^{3-} + H^+$	6.4		[79]
B2.7	$HForm \rightarrow Form^- + H^+$	3.75		[291]
B2.8	$HGly \rightarrow Gly^- + H^+$	3.83		[79, 291]

(*continued*)

No.	Dissociation reactions	$pK_a = -\log K_a$	$T; I(M)$	Reference
B2.9	$H_2Mal \rightarrow HMal^- + H^+$	2.83, 2.85		[79, 291]
B2.10	$HMal^- \rightarrow Mal^{2-} + H^+$	5.70		[79, 291]
B2.11	$H_2Oxa \rightarrow HOxa^- + H^+$	1.19		[295]
		1.27		[291]
B2.12	$HOxa^- \rightarrow Oxa^{2-} + H^+$	4.21		[295]
		4.27		[291]
B2.13	$HO_2^\bullet \rightarrow O_2^{\bullet -} + H^+$	4.8		[296]
B2.14	$^\bullet HO \rightarrow ^\bullet O^- + H^+$	11.5		[297]
		11.9		[298]
B2.15	$HO_3^\bullet \rightarrow O_3^{\bullet -} + H^+$	8.2		[299]
B2.16	$H_2O_2 \rightarrow HO_2^- + H^+$	11.7		[261]

*Ace = acetate (CH_3COO^-), Cit = citrate ($C_3H_5O(COO)_3^{3-}$), Form = formate ($HCOO^-$), Gly = glycolate (CH_2OHCOO^-), Mal = malonate ($CH_2(COO)_2^{2-}$), Oxa = oxalate ($C_2O_4^{2-}$).

B3 *Complex formation constants for Fe(II) and inorganic anions at 25 °C, $I = 0\,M$*

No.	Complexes	$\log \beta^a$	Condition	Reference
B3.1	$Fe^{II}OH^+$	4.5		[79]
		4.6	$I = 0\,M^b$	[300, 301]
		5.6	20–25 °C, $I \sim 0\,M$	[291]
B3.2	$Fe^{II}(OH)_2$	7.4		[79]
		7.5	$I = 0\,M^b$	[300, 301]
		9.8	20–25 °C, $I \sim 0\,M$	[291]
B3.3	$Fe^{II}(OH)_3^-$	9.7	20–25 °C, $I \sim 0\,M$	[291]
		11.0		[79]
		13.5	$I = 0\,M^b$	[300] [301]
B3.4	$Fe^{II}(OH)_4^{2-}$	8.6	20–25 °C, $I \sim 0\,M$	[291]
		10.0	$I = 0\,M^b$	[300] [301]
B3.5	$Fe^{II}CO_3$	5.5		[302]
		5.7		[303]
B3.6	$Fe^{II}(CO_3)_2^{2-}$	7.2		[302]
		7.5		[303]
B3.7	$Fe^{II}HCO_3^+$	11.8		[303]
B3.8	$Fe^{II}(CO_3)(OH)^-$	10.0		[303]
B3.9	$Fe^{II}Cl^+$	0.3		[303]
		0.36	20–25 °C, $I \sim 0\,M$	[291]
B3.10	$Fe^{II}(CN)_6^{4-}$	35.4		[79]
B3.11	$Fe^{II}F^+$	1.4		[79]
B3.12	$Fe^{II}HPO_4$	16.0		[79]
B3.13	$Fe^{II}H_2PO_4^+$	22.3		[79]
B3.14	$Fe^{II}SO_3$	8.4		[114]
		9.9		[304]
B3.15	$Fe^{II}SO_4$	2.2		[79]
		2.25		[81]
		2.4		[303]

[a] Complex formation constant (or stability constant) $\beta = [M_V(H)_W(OH)_X L_Y^{Z\pm}]/\{[M^{a+}]^V [L^{b-}]^Y [OH^-]^X [H^+]^W\}$, all concentrations in the unit of M.
[b] Corrected to 0 M ionic strength by Uchimiya *et al.* 2006 [301]. For temperature, please refer to Martell *et al.* 2004 [300].

B4 Complex formation constants for Fe(II) and organic anions at 25 °C, $I = 0\,M$*

No.	Complexes	log β^a	Condition	Reference
B4.1	$Fe^{II}Ace^{+}$	1.4		[79]
		3.2	I = 0.1 M	[291]
B4.2	$Fe^{II}(Ace)_2$	6.1	I = 0.1 M	[291]
B4.3	$Fe^{II}(Ace)_3^{-}$	8.3	I = 0.1 M	[291]
B4.4	$Fe^{II}Cit^{-}$	5.7		[79]
B4.5	$Fe^{II}HCit$	9.9		[79]
B4.6	$Fe^{II}EDA^{2+}$	4.3		[79, 291]
B4.7	$Fe^{II}(EDA)_2^{2+}$	7.7		[79, 291]
B4.8	$Fe^{II}(EDA)_3^{2+}$	9.7		[79, 291]
B4.9	$Fe^{II}EDTA^{2-}$	14.3	20–25 °C, I ~ 0 M	[291]
		16.1		[79]
B4.10	$Fe^{II}HEDTA^{-}$	19.3		[79]
B4.11	$Fe^{II}OHEDTA^{3-}$	20.4		[79]
B4.12	$Fe^{II}(OH)_2EDTA^{4-}$	23.7		[79]
B4.13	$Fe^{II}Glu$	4.6		[79]
B4.14	$Fe^{II}Gly^{+}$	1.9		[79]
B4.15	$Fe^{II}Mal$	3.0	I = 0 M[b]	[300, 301]
B4.16	$Fe^{II}(Mal)_2^{2-}$	4.0	I = 0 M[b]	[300, 301]
B4.17	$Fe^{II}Oxa$	2.9	20–25 °C, I ~ 0 M	[291]
		3.9	I = 0 M[b]	[300] [301]
B4.18	$Fe^{II}(Oxa)_2^{2-}$	4.5	20–25 °C, I ~ 0 M	[291]
		5.9	I = 0 M[b]	[300, 301]
B4.19	$Fe^{II}(Oxa)_3^{4-}$	5.2	20–25 °C, I ~ 0 M	[291]
		5.2	I = 0 M[b]	[300, 301]
B4.20	$Fe^{II}Phtha$	2.7	I = 0.7 M	[305]
B4.21	$Fe^{II}Sal$	6.5	I = 0.7 M	[305]
		7.4		[79]
B4.22	$Fe^{II}(Sal)_2^{2-}$	11.1	I = 0.7 M	[305]
		12.1		[79]

*Ace = acetate (CH_3COO^-), Cit = citrate ($C_3H_5O(COO)_3^{3-}$), EDA = ethylene diamine ($H_2NC_2H_4NH_2$), EDTA = ethylenediaminetetraacetate ($C_6H_{12}N_2(COO^-)_4^{4-}),^{-}$), Glu = glutamate ($^{-}OOC(NH_2)C_3H_5COO^-$), Gly = glycolate ($CH_2OHCOO^-$), Lac = lactate ($CH_3CH(OH)COO^-$), Mal = malonate ($CH_2(COO)_2^{2-}$), Oxa = oxalate ($C_2O_4^{2-}$), Phtha = o-phthalate ($C_6H_4(COO^-)_2$), Sal = salicylate ($C_6H_4(Od)COO^-$).

[a] Complex formation constant $\beta = [M_V(H)_W(OH)_X L_Y^{Z\pm}]/[M^{a+}]^V[L^{b-}]^Y[OH^-]^X[H^+]^W$, all concentrations in the unit of M.

[b] Corrected to 0 M ionic strength by Uchimiya *et al.* 2006 [301]. For temperature, please refer to Martell *et al.* 2004 [300].

$$FeOH^{2+} + HSO_3^- \longrightarrow FeOHSO_3H^+ \qquad \text{[Fe(III)-S(IV)-1]}$$

$K = 8.5 \times 10^2\ M^{-1}$

Betterton, 1993.

B5 *Complex formation constants for Fe(III) and inorganic anions at 25 °C, $I = 0\,M$*

No.	Complexes	log β^{a}	Condition	Reference
B5.1	$Fe^{III}OH^{2+}$	11.3	$I = 1.0\,M$	[45]
		11.8^{b}		[306]
		11.8^{b}	$I = 0.1\,M$	[43]
		11.8	$I = 0\,M^{b}$	[300, 301]
		11.8^{b}		[302]
		11.9	20–25 °C, $I \sim 0\,M$	[291]
B5.2	$Fe^{III}(OH)_2^{+}$	21.2	20–25 °C, $I \sim 0\,M$	[291]
		21.7	$I = 1.0\,M$	[307]
		22.3^{b}	$I = 0.1\,M$	[43]
		22.3^{b}		[306]
		22.5		[302]
		23.4	$I = 0\,M^{b}$	[300, 301]
B5.3	$Fe^{III}(OH)_3$	28.4	$I = 0\,M^{b}$	[300, 301]
		29.7	20–25 °C, $I \sim 0\,M$	[291]
		30.2		[302]
B5.4	$Fe^{III}(OH)_4^{-}$	34.4		[300, 301], [302, 79]
B5.5	$Fe_2^{III}(OH)_2^{4+}$	25.0		[79]
		25.1	$I = 0\,M^{b}$	[300, 301]
		25.2^{b}	$I = 1\,M$	[138]
B5.6	$Fe_3^{III}(OH)_4^{5+}$	48.4	$I = 1.0\,M$	[307]
		49	$I = 1.0\,M$	[307]
		49.7^{b}	$I = 0\,M^{b}$	[301]
B5.7	$Fe^{III}Br^{2+}$	0.6		[79]
B5.8	$Fe^{III}Cl^{2+}$	1.28		[302]
		1.3		[302]
		1.48	20–25 °C, $I \sim 0\,M$	[291]
		1.5		[79]
B5.9	$Fe^{III}Cl_2^{+}$	1.16		[302]
		1.5	20–25 °C, $I \sim 0\,M$	[291]
		2.1		[79]
B5.10	$Fe^{III}Cl_3$	2.0	20–25 °C, $I \sim 0\,M$	[291]
B5.11	$Fe^{III}(CN)_6^{3-}$	43.6		[79]
B5.12	$Fe^{III}F^{2+}$	5.3	20–25 °C, $I \sim 0\,M$	[291]
		6.0		[79]
B5.13	$Fe^{III}F_2^{+}$	9.3	20–25 °C, $I \sim 0\,M$	[291]
		10.6		[79]
B5.14	$Fe^{III}F_3$	12.1	20–25 °C, $I \sim 0\,M$	[291]
		13.7		[79]
B5.15	$Fe^{III}HPO_4^{+}$	22.5		[79]

(*continued*)

No.	Complexes	log β[a]	Condition	Reference
B5.16	$Fe^{III}H_2PO_4^{2+}$	23.9		[79]
B5.17	$Fe^{III}HSiO_3^{2+}$	22.7		[79]
B5.18	$Fe^{III}SO_3^{+}$	6.6	I = 0.4 M, pH ~ 2	[136]
		6.8		[139]
		7.2	I = 1.0 M	[220]
		7.8	I = 0.1 M	[308]
B5.19	$Fe^{III}(SO_3)_2^{-}$	16.5	I = 0.1 M, pH 1–3	[43]
		17.6	I = 0.1 M	[308]
B5.20	$Fe^{III}(SO_3)_3^{3-}$	27	I = 0.1 M	[308]
B5.21	$Fe^{III}(HSO_3)^{2+}$	8.9		[139]
		9.1		[26]
B5.22	$Fe^{III}OH(SO_3)$	19.1		[26]
		19.1–19.7	I = 0.4 M, pH ~ 2	[136]
		21.7	I = 0.1 M, pH1–3	[43]
B5.23	$Fe^{III}OH(HSO_3)^{+}$	21.8		[26, 214]
		21.9		[139]
B5.24	$Fe_2^{III}OH(SO_3)^{3+}$	36.1	I = 1.0 M	[45]
B5.25	$Fe^{III}S_2O_3^{-}$	2.1	20–25 °C, I ~ 0 M	[291]
		3.3		[79]
B5.26	$Fe^{III}S_2O_3^{-}$	2.1	20–25 °C, I ~ 0 M	[291]
		3.3		[79]
B5.27	$Fe^{III}SO_4^{+}$	2.3	I = 0.5 M	[309]
		2.4		[141]
		4.0		[79, 81]
		4.3		[310, 302]
B5.28	$Fe^{III}(SO_4)_2^{-}$	5.4		[79, 81]
		6.1		[302]
B5.29	$Fe^{III}H(SO_4)_2$	8.1		[311]

[a] Complex formation constant (or stability constant) $\beta = [M_V(H)_W(OH)_X L_Y^{Z\pm}]/[M^{a+}]^V[L^{b-}]^Y[OH^-]^X[H^+]^W$, all concentrations in the unit of M.

[b] Corrected to 0 M ionic strength by Uchimiya *et al.* 2006 [301]. For temperature, please refer to Martell *et al.* 2004 [300].

B6 *Complex formation constants for Fe(III) and organic anions at 25 °C, $I = 0\,M$**

No.	Complexes	log β[a]	Condition	Reference
B6.1	$Fe^{III}Ace^{2+}$	3.2	20 °C, I = 1 M	[291]
		4.0		[79]
B6.2	$Fe^{III}(Ace)_2^{+}$	7.6		[79]
B6.3	$Fe^{III}(Ace)_3$	9.6		[79]
B6.4	$Fe^{III}Cit$	13.5		[79]
B6.5	$Fe_2^{III}(OH)_2(Cit)_2^{2-}$	56.3		[79]

(*continued*)

No.	Complexes	log β^a	Condition	Reference
B6.6	$Fe^{III}EDTA^-$	24.2	20–25 °C, I ∼ 0 M	[291]
		27.7		[79]
B6.7	$Fe^{III}HEDTA$	29.2		[79]
B6.8	$Fe^{III}OHEDTA^{2-}$	33.8		[79]
B6.9	$Fe^{III}(OH)_2EDTA^{3-}$	37.7		[79]
B6.10	$Fe^{III}Glu^+$	13.8		[79]
B6.11	$Fe^{III}Gly^{2+}$	3.7		[79]
B6.12	$Fe^{III}OHGly^+$	19.6		[79]
B6.13	$Fe^{III}OH(Gly)_2$	22.3		[79]
B6.14	$Fe^{III}OH(Gly)_3^-$	23.8		[79]
B6.15	$Fe^{III}Lac^{2+}$	7.1	20–25 °C, I ∼ 0 M	[291]
B6.16	$Fe^{III}Mal^+$	9.1	I = 0 M^b	[300, 301]
		9.3		[79]
B6.17	$Fe^{III}(Mal)_2^-$	15.4	I = 0 M^b	[300, 301]
B6.18	$Fe^{III}(Mal)_3^{3-}$	18.8	I = 0 M^b	[300, 301]
B6.19	$Fe^{III}Oxa^+$	8.8	I = 0 M^b	[300, 301]
		9.4	20–25 °C, I ∼ 0 M	[291]
		9.4		[312]
B6.20	$Fe^{III}(Oxa)_2^-$	15.4	I = 0 M^b	[300, 301]
		16.2	20–25 °C, I ∼ 0 M	[291]
		16.2		[312]
B6.21	$Fe^{III}(Oxa)_3^{3-}$	19.8	I = 0 M^b	[300, 301]
		20.2	20–25 °C, I ∼ 0 M	[291]
		20.8		[312]
B6.22	$Fe^{III}HOxa^{2+}$	4.4		[313]
B6.23	$Fe^{III}C_6H_5O^{2+}$	7.6	I = 0.1 M	[107]
B6.24	$Fe^{III}Sal^+$	16.3	I = 0.7 M	[305]
		17.6		[79]
B6.25	$Fe^{III}(Sal)_2^-$	28.6		[79]
		28.8	I = 0.7 M	[305]
B6.26	$Fe^{III}(Sal)_3^{3-}$	36.2		[79]
B6.27	$Fe^{III}HSal^{2+}$	4.1	I = 0.7 M	[305]

*Ace = acetate (CH_3COO^-), Cit = citrate ($C_3H_5O(COO)_3^{3-}$), EDTA = ethylenediaminetetraacetate ($C_6H_{12}N_2(COO^-)_4^{4-}$), Glu = glutamate ($^-OOC(NH_2)C_3H_5COO^-$), Gly = glycolate ($CH_2OHCOO^-$), Lac = lactate ($CH_3CH(OH)COO^-$), Mal = malonate ($CH_2(COO)_2^{2-}$), Oxa = oxalate ($C_2O_4^{2-}$), Sal = salicylate ($C_6H_4(O^-)COO^-$).

[a] Complex formation constant $\beta = [M_V(H)_W(OH)_X L_Y^{Z\pm}]/[M^{a+}]^V[L^{b-}]^Y[OH^-]^X[H^+]^W$, all concentrations in the unit of M.

[b] Corrected to 0 M ionic strength by Uchimiya *et al.* 2006 [301]. For temperature, please refer to Martell *et al.* 2004 [300].

B7 *Reduction potential of sulphur oxide radicals and molecules at* 25 °C*

No.	Oxidant State	Half cell reaction	$E_H(V)$	Condition	Reference
B7.1	S(IX)	$SO_5^{\bullet -} + e^- + H^+ \rightarrow HSO_5^-$	1.1	$pH = 7$	[58]
B7.2		$SO_5^{\bullet -} + e^- \rightarrow SO_5^{2-}$	0.81	$pH = 11$, 21 °C	[57]
B7.3	S(VIII)	$HSO_5^- + 2e^- + 2H^+ \rightarrow HSO_4^- + H_2O$	1.81	$pH = 0$	[106]
			1.84		[279]
B7.4		$HSO_5^- + 2e^- + H^+ \rightarrow SO_4^{2-} + H_2O$	1.75	$pH = 0$	[36]
B7.5	S(VII)	$SO_4^{\bullet -} + e^- \rightarrow SO_4^{2-}$	2.43		[314]
			2.6	$pH = 0$	[315]
B7.6		$S_2O_8^{2-} + e^- \rightarrow S_2O_8^{3-}$	~0.1		[316]
B7.7		$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	2.0	$pH = 0$	[317]
B7.8		$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^-$	2.1	$pH = 0$	[292]
B7.9	S(VI)	$SO_4^{2-} + H_2O + e^- \rightarrow SO_3^{\bullet -} + 2OH^-$	−2.47	$pH > 7.2$	[58]
B7.10		$SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-$	−0.93	$pH = 0$	[292]
B7.11		$2SO_4^{2-} + 4H^+ + 2e^- \rightarrow S_2O_6^{2-} + 2H_2O$	−0.22	$pH = 0$	[292]
B7.12		$SO_3 + e^- \rightarrow SO_3^{\bullet -}$	0.25		[279]
B7.13		$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.17	$pH = 0$	[292]
B7.14		$HSO_4^- + 2H^+ + 2e^- \rightarrow H_2SO_3 + OH^-$	0.10		[318]
B7.15	S(V)	$SO_3^{\bullet -} + e^- = SO_3^{2-}$	0.63	$pH > 7$	[58]
			0.84	$pH = 3.6$	[58]
			0.73	$pH = 11.5$, 21 °C	[57]
			0.72	$pH = 0$	[319]
B7.16		$S_2O_6^{2-} + 4H^+ + 2e^- \rightarrow 2H_2SO_3$	0.56		[292]
B7.17	S(IV)	$2SO_3^{2-} + 2H_2O + 2e^- \rightarrow S_2O_4^{2-} + 4OH^-$	−1.12	$pH = 0$	[292]
B7.18		$2SO_3^{2-} + 3H_2O + 4e^- \rightarrow S_2O_3^{2-} + 6OH^-$	−0.57	$pH = 0$	[292]
B7.19		$2H_2SO_3 + H^+ + 2e^- \rightarrow HS_2O_4^- + 2H_2O$	−0.06	$pH = 0$	[292]
B7.20	S(V/II)	$S_2O_3^{\bullet -} + e^- \rightarrow S_2O_3^{2-}$	1.34	$pH = 0$	[319]
B7.21		$S_4O_6^{2-} + 2e^- + 2H^+ \rightarrow 2HS_2O_3^-$	0.1	$pH = 0$	[318]
B7.22	S(IX/IV)	$S_4O_6^{\bullet 3-} + e^- \rightarrow 2S_2O_3^{2-}$	1.07	$pH \geq 8.8$	[57]
			1.13	$pH = 0$	[319]

*E_H of $SO_5^{\bullet -}$ and $SO_3^{\bullet -}$ at other pH can be calculated from: $E_{pH} = E_{pH=0} + 0.059 \log\{(K_{a1}K_{a2} + K_{a1}[H^+] + [H^+]^2)/(K_{ar} + [H^+])\}$, where E_{pH} = redox potential at pH of interest, K_{a1}, K_{a2} are the 1st and 2nd acid dissociation constants of H_2SO_x, K_{ar} = acid dissociation constant of $HSO_x^{\cdot}$ radical estimated to be 10^{-2} M. For reference, see Huie and Neta (1984) [58] and Das *et al.* (1999) [57].

B8 *Standard reduction potential of important aqueous oxidants at 25 °C*

No.	Half cell reaction	E^o_H(V)	Reference
B8.1	$HO^\bullet + e^- \rightarrow OH^-$	1.9	[297]
		2.02	[217]
B8.2	$HO^\bullet + e^- + H^+ \rightarrow H_2O$	2.7	[297]
B8.3	$O_3 + e^- \rightarrow O_3^-$	1.0	[80]
B8.4	$^1O_2 + e^- \rightarrow O_2^{\bullet -}$	0.83	[80]
B8.5	$^3O_2 + e^- \rightarrow O_2^{\bullet -}$	−0.16	[80]
B8.6	$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$	1.77	[79]
B8.7	$HO_2^\bullet + e^- \rightarrow HO_2^-$	0.75	[80]
B8.8	$O_2^{\bullet -} + e^- + H^+ \rightarrow HO_2^-$	1.03[a]	[80]
B8.9	$CO_3^{\bullet -} + e^- \rightarrow CO_3^{2-}$	1.6	[80]
B8.10	$Cl_2^{\bullet -} + e^- \rightarrow 2Cl^-$	2.09	[320]
B8.11	$ClO_2^\bullet + e^- \rightarrow ClO_2^-$	0.93	[279]
B8.12	$Br_2^{\bullet -} + e^- \rightarrow 2Br^-$	1.62	[320]
B8.13	$I_2^{\bullet -} + e^- \rightarrow 2I^-$	1.03	[320]
B8.14	$N_3^\bullet + e^- \rightarrow N_3^-$	1.35	[320]
B8.15	$NO_2 + e^- \rightarrow NO_2^-$	1.03	[270]
B8.16	$NO_3 + e^- \rightarrow NO_3^-$	2.3	[270]
B8.17	$ArO^\bullet + e^- \rightarrow ArO^-$	0.79	[80]

[a] Calculated from acid dissociation constant pK_a of $HO_2^\bullet = 4.8$, according to Kwan *et al.* 2003 [259].

B9 ΔG^o_f *and* ΔH^o_f *of some sulphur oxide radicals and ions at 25 °C*

No.	Aqueous species	ΔG^o_f (kJ mol^{-1})	ΔH^o_f (kJ mol^{-1})	Reference
B9.1	H_2O	−237.13		[321]
			−285.83	[78]
B9.2	HSO_3^-	−527.7		[321]
B9.3	SO_4^{2-}	−744.5		[321]
			−909.27	[78]
B9.4	$S_2O_6^{2-}$	−1004	−1198.4	[322]
B9.5	$S_2O_7^{2-}$	−1193		[121]
B9.6	$S_2O_8^{2-}$	−1114.9		[321]
			−1344.7	[322]
B9.7	HSO_5^-	−638		[323]
B9.8	$SO_2^{\bullet -}$		−326.5	[322]
B9.9	$SO_3^{\bullet -}$	−426		[58]
			−501.9	[322]
B9.10	$SO_4^{\bullet -}$	−510.6		[279]
			−607.7	[322]
B9.11	$SO_5^{\bullet -}$	−493		[58]
		−486.6	−605.4	[322]

B10 ΔE^o_H *for the formation of* $SO_3^{\bullet-}$ *from* Me^{n+}*-induced S(IV) oxidation at* $25\,^\circ C$

No.	$^aMe^{n+}/Me^{(n-1)+}$	$E^o_H(Me^{n+}/Me^{(n-1)+})(V)$	$\Delta E^o_H(V)^b$	$\Delta E^o_H(V)^c$
B10.1	Ag^{3+}/Ag^{2+}	1.8^d	0.96	0.66
B10.2	Ag^{2+}/Ag^{+}	1.99^d	1.15	0.85
B10.3	Ce^{4+}/Ce^{3+}	1.72^e	0.88	0.58
B10.4	Co^{3+}/Co^{2+}	1.92^e	1.04	0.74
B10.5	Cr^{3+}/Cr^{2+}	-0.41^e	−1.25	−0.95
B10.6	Cu^{3+}/Cu^{2+}	2.4^e	1.56	1.26
B10.7	Cu^{2+}/Cu^{+}	0.15^e	−0.69	−0.99
B10.8	Fe^{3+}/Fe^{2+}	0.77^e	−0.07	−0.37
B10.9	Mn^{2+}/Mn^{+}	-4.46^f	−5.3	−5.6
B10.10	Mn^{3+}/Mn^{2+}	1.54^e	0.7	0.4
B10.11	Ni^{3+}/Ni^{2+}	2.3^d	1.46	1.16
B10.12	Ti^{3+}/Ti^{2+}	-0.9^e	−1.74	−2.04
B10.13	V^{3+}/V^{2+}	-0.26^e	−1.1	−1.4

[a] $Me^{n+} + e^- \rightarrow Me^{(n-1)+}$.

[b] ΔE^o_H for $Me^{n+} + SO_3^{2-} \rightarrow Mn^{(n-1)+} + SO_3^{\bullet-}$, with $E^o_H(SO_3^{2-} \rightarrow SO_3^{\bullet-} + e^-) \sim -0.84\,V$.

[c] ΔE^o_H for $Me^{n+} + SO_3^{2-} \rightarrow Mn^{(n-1)+} + SO_3^{\bullet-}$, with $E^o_H(SO_3^{2-} \rightarrow SO_3^{\bullet-} + e^-) - 1.14\,V$ is the pH-corrected redox potential at $[H^+] = 1\,M$ from $-0.84\,V$(at pH 3.6) (Huie and Neta) and $-0.73\,V$ (at pH 11.5) (Das *et al.* 1999) using the equation beneath B.7.

[d] ref. [318].

[e] ref. [292].

[f] ref. [141].

Appendix C: Kinetic data related to aqueous Fe-S(IV)-O$_2$ system

C1 *Rate constants for elementary reactons involving S(IV) transformations*

No.	Elementary reaction	$k(M^{-1}s^{-1})$; (E_a in kJ mol^{-1})	Condition	Reference
C1.1	$HSO_3^- + OH^\bullet \rightarrow SO_3^{\bullet-} + H_2O$	2.7×10^9	pH 4.5	[324]
		2.7×10^9		[325]
		4.2×10^9		[217]
		4.5×10^9		[326]
		9.5×10^9		[4]
C1.2	$SO_3^{2-} + OH^\bullet \rightarrow SO_3^{\bullet-} + OH^-$	2.7×10^9	pH 4.5	[304]
		4.1×10^9	pH 9.0	[304]
		4.5×10^9	pH 4.4	[327]
		4.6×10^9	pH 8.5	[217]
		5.2×10^9	pH 11.2	[327]
		5.4×10^9		[326]
		5.5×10^9		[4]
C1.3	$HSO_3^- + O_3 \rightarrow HSO_4^- + O_2$	$3.7 \times 10^5 (E_a = 46)$		[328]
C1.4	$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$	$1.5 \times 10^9 (E_a = 44)$		[328]
C1.5	$SO_2 + O_3(+H_2O) \rightarrow HSO_4^- + O_2 + H^+$	2.4×10^4		[328]

(*continued*)

No.	Elementary reaction	$k(M^{-1}s^{-1})$; (E_a in $kJ\,mol^{-1}$)	Condition	Reference
C1.6	$HSO_3^- + HO_2^\bullet \rightarrow SO_5^{\bullet-}$ + products	$<2 \times 10^1$		[272]
C1.7	$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H_2O + H^+$	$\sim 1 \times 10^3$		[144]
		$6.9 \times 10^7 (E_a = 33)$		[329]
C1.8	$HSO_3^- + CH_3OOH \rightarrow SO_4^{2-} + CH_3OH + H^+$	$1.8 \times 10^7 (E_a = 32)$		[329]
C1.9	$2HSO_3^- \rightarrow S_2O_5^{2-} + H_2O$	7×10^2	25 °C	[96]
C1.10	$HSO_3^- + SO_4^{\bullet-} \rightarrow SO_4^{2-} + SO_3^{\bullet-} + H^+$	1.3×10^8		[55]
		4.6×10^8		[327]
		5.3×10^8	$pH > 7$	[55]
		6.8×10^8	pH 4, $I = 0\,M$	[185]
		7.5×10^8		[330]
		2.0×10^9	pH 8.7	[327]
		2.5×10^9		[269]
C1.11	$SO_3^{2-} + SO_4^{\bullet-} \rightarrow SO_4^{2-} + SO_3^{\bullet-}$	$3.1 \times 10^8 (E_a = 9.6)$	$I = 0\,M$	[184]
		$3.2 \times 10^8 (E_a = 10)$		[331]
		5.5×10^8	pH 8.0	[38]
C1.12	$HSO_3^- + SO_5^{\bullet-} \rightarrow HSO_5^- + SO_3^{\bullet-}$ $\rightarrow H^+ + SO_4^{2-} + SO_4^{\bullet-}$	3.6×10^3		[272]
C1.13	$HSO_3^- + SO_5^{\bullet-} \rightarrow HSO_5^- + SO_3^{\bullet-}$	8.5×10^3		[144]
		8.6×10^3		[185]
		2.5×10^4	pH 4.9	[327]
		7.5×10^4		[332]
		$<3.0 \times 10^5$		[327]
		3.0×10^6	pH 6.8	[58]
		1.3×10^7	pH 8.7	[327]
C1.14	$SO_3^{2-} + SO_5^{\bullet-}(+H^+) \rightarrow HSO_5^- + SO_3^{\bullet-}$	2.1×10^5	acidic	[185]
		3.0×10^6		[38]
		3.8×10^6		[332]
C1.15	$SO_3^{2-} + SO_5^{\bullet-} \rightarrow SO_5^{2-} + SO_3^{\bullet-}$	3.6×10^5	pH 9	[185]
C1.16	$HSO_3^- + SO_5^{\bullet-} \rightarrow HSO_4^- + SO_4^{\bullet-}$ (or $HSO_3^- + SO_5^{\bullet-} \rightarrow H^+ + SO_4^{2-} + SO_4^{\bullet-}$)	3.6×10^2		[185]
		2.5×10^4	pH 4.9	[332]
		$<3.0 \times 10^5$		[327]
		1.3×10^7		[67]
		3.0×10^8		[144]
C1.17	$SO_3^{2-} + SO_5^{\bullet-} \rightarrow SO_4^{2-} + SO_4^{\bullet-}$	1.3×10^5		[163]
		1.4×10^5	pH 9	[185]
C1.18	$SO_3^{2-} + SO_5^{\bullet-}(+H^+) \rightarrow HSO_4^- + SO_4^{\bullet-}$	7.5×10^4		[327]
		5.5×10^6		[185]
		9.0×10^6		[332]
		1.0×10^7		[38]
C1.19	$HSO_3^- + HSO_5^- \rightarrow 2SO_4^{2-} + 2H^+$	$\sim 1 \times 10^3$		[144]
C1.20	$HSO_3^- + HSO_5^- + H^+ \rightarrow 2HSO_4^- + H^+$	5.6×10^6		[217]
C1.21	$HSO_3^- + HSO_5^- \rightarrow 2HSO_4^-$	3.5×10^2	pH 8.0	[38]
		9.1×10^3	pH 2.9	[217]
		2.0×10^4	pH 2.5	[217]
		7.9×10^4	pH 1.5	[217]
		7.5×10^5		[12]
C1.22	$HSO_3^- + NO_2 \rightarrow NO_2^- + HSO_3^\bullet$	1.5×10^4	25 °C	[333]

(*continued*)

No.	Elementary reaction	k(M^{-1}s^{-1}); (E$_a$ in kJ mol^{-1})	Condition	Reference
		2.8×10^4	55 °C	[12]
C1.23	$SO_3^{2-} + NO_2 \rightarrow NO_2^- + SO_3^{\bullet-}$	6.6×10^5	25 °C	[333]
		1.1×10^6	55 °C	[12]
C1.24	$S(IV) + 2NO_2(+OH^-)$	1.1×10^7	pH 5.3, I = 0.5 M	[232]
	$\rightarrow 2NO_2^- + S(VI) + H^+$	2.9×10^7	pH 13, I = 0.5 M	[232]
C1.25	$HSO_3^- + Cl^\bullet \rightarrow Cl^- + H^+ + SO_3^{\bullet-}$	1.0×10^9		[54]
C1.26	$HSO_3^- + Cl_2^{\bullet-} \rightarrow 2Cl^- + H^+ + SO_3^{\bullet-}$	$1.7 \times 10^8 (E_a = 3)$		[334]
		1.8×10^8		[335]
		$4.7 \times 10^8 (E_a = 9)$	25 °C, I = 0.1 M	[320]
C1.27	$SO_3^{2-} + Cl_2^{\bullet-} \rightarrow 2Cl^- + SO_3^{\bullet-}$	6.2×10^7		[334]
		5.0×10^8		[54]
C1.28	$HSO_3^- + Br_2^{\bullet-} \rightarrow 2Br^- + H^+ + SO_3^{\bullet-}$	$6.3 \times 10^7 (E_a = 6.5)$	25 °C, I = 0.1 M	[320]
C1.29	$SO_3^{2-} + Br_2^{\bullet-} \rightarrow 2Br^- + SO_3^{\bullet-}$	$2.2 \times 10^8 (E_a = 5.4)$	25 °C, I = 0.1 M	[320]
C1.30	$HSO_3^- + I_2^{\bullet-} \rightarrow 2I^- + H^+ + SO_3^{\bullet-}$	$1.4 \times 10^6 (E_a = 19)$	25 °C, I = 0.1 M	[320]
C1.31	$SO_3^{2-} + I_2^{\bullet-} \rightarrow 2I^- + SO_3^{\bullet-}$	$1.7 \times 10^8 (E_a = 12)$	25 °C, I = 0.1 M	[320]
C1.32	$HSO_3^- + CO_3^{\bullet-} \rightarrow CO_3^{2-} + H^+ + SO_3^{\bullet-}$	Est1 $\times 10^7$		[69]
C1.33	$SO_3^{2-} + CO_3^{\bullet-} \rightarrow CO_3^{2-} + SO_3^{\bullet-}$	$5.0 \times 10^6 (E_a = 3.9)$		[336]
C1.34	$HSO_3^- + Mn^{3+} \rightarrow Mn^{2+} + H^+ + SO_3^{\bullet-}$	1.3×10^6		[76]
C1.35	$SO_3^{2-} + Cu^{2+} \rightarrow Cu^+ + SO_3^{\bullet-}$	3.6×10^{-3}		[126]
C1.36	$[Cu^{II}S^{IV}O_3Cu^{II}]^{2+} \rightarrow [Cu^{II}S^{V}O_3Cu^{I}]^{2+}$	$5.7 \times 10^{-3}\ s^{-1}$		[72]

C2 *Rate constants for elementary reactons involving* $SO_X^{\bullet-}$ *and* SO_5^{2-} *transformations*

No.	Elementary reaction	k (M^{-1} s^{-1}); (E$_a$ in kJ mol^{-1})	Condition	Reference
C2.1	$SO_3^{\bullet-} + O_2 \rightarrow +SO_5^{\bullet-}$	1.1×10^9		[269]
		1.5×10^9		[217]
		2.5×10^9		[185]
C2.2	$SO_4^{\bullet-} + {}^\bullet OH \rightarrow HSO_5^-$	9.0×10^9	I = 0 M	[185]
		1.0×10^{10}	25 °C	[54]
C2.3	$SO_4^{\bullet-} + {}^\bullet H \rightarrow +HSO_4^-$	6.8×10^9	I = 0 M	[185]
C2.4	$SO_4^{\bullet-} + O_2^{\bullet-} \rightarrow +SO_4^{2-} + O_2$	3.5×10^9		[331]
		4.0×10^9		[185]
C2.5	$SO_4^{\bullet-} + HO_2^{\bullet-} \rightarrow +SO_4^{2-} + H^+ + O_2$	3.5×10^9		[331]
C2.6	$SO_4^{\bullet-} + H_2O_2 \rightarrow +SO_4^{2-} + H^+ + HO_2^\bullet$	1.2×10^7		[337]
		2.8×10^7		[331]
C2.7	$SO_4^{\bullet-} + H_2O \rightarrow +HSO_4^- + {}^\bullet OH$	9.3×10^0		[338]
C2.8	$SO_4^{\bullet-}(+H_2O) \rightarrow {}^\bullet OH + SO_4^{2-}$	$4.4 \times 10^2\ s^{-1}$		[339]
		$5.0 \times 10^2\ s^{-1}$		[325]
C2.9	$SO_4^{\bullet-} + H_2O \rightarrow +SO_4^{2-} + H^+ + {}^\bullet OH$	$1.1 \times 10^1 (E_a = 9.2)$		[338]
C2.10	$SO_4^{\bullet-} + OH^- \rightarrow +SO_4^{2-} + {}^\bullet OH$	1.4×10^7		[338]
		2.0×10^7	I = 0 M	[335]
		6.5×10^7		[55]
		7.3×10^7	pH 6.8	[276]

(*continued*)

No.	Elementary reaction	k ($M^{-1}\,s^{-1}$); (E_a in kJ mol^{-1})	Condition	Reference
C2.11	$SO_4^{\bullet-} + S_2O_8^{2-} \rightarrow +SO_4^{2-} + S_2O_8^{\bullet-}$	6.1×10^5		[325]
		6.3×10^5		[338]
C2.12	$SO_4^{\bullet-} + HSO_5^- \rightarrow +HSO_4^- + SO_5^{\bullet-}$	1.0×10^6	25 °C	[54]
C2.13	$SO_4^{\bullet-} + SO_5^{2-} \rightarrow SO_4^{2-} + SO_5^{\bullet-}$	1.0×10^8	25 °C	[54]
C2.14	$SO_4^{\bullet-} + HSO_3^- \rightarrow SO_4^{2-} + SO_3^{\bullet-} + H^+$	1.3×10^8		[55]
		4.6×10^8		[327]
		5.3×10^8	$pH > 7$	[55]
		6.8×10^8	pH 4, $I = 0\,M$	[185]
		7.5×10^8		[330]
		2.0×10^9	pH 8.7	[327]
		2.5×10^9		[269]
C2.15	$SO_4^{\bullet-} + SO_3^{2-} \rightarrow SO_4^{2-} + SO_3^{\bullet-}$	$3.1 \times 10^8 (E_a = 9.6)$	$I = 0\,M$	[185]
		$3.2 \times 10^8 (E_a = 10)$		[331]
		5.5×10^8	pH 8.0	[38]
C2.16	$Cr^{3+} + SO_4^{\bullet-} \leftrightarrow [Cr^{III}(S^{VII}O_4^{\bullet})]^-$	$K = 7.6 \times 10^2$	pH 3	[268]
		$K = 4.2 \times 10^3$	pH 3.7	[268]
C2.17	$[Cr^{III}(S^{VII}O_4^{\bullet})]^- \rightarrow Cr^{IV} + SO_4^{2-}$	$k_{ET} = 2.3 \times 10^4$	pH 3	[268]
		$k_{ET} = 1.2 \times 10^4$	pH 3.7	[268]
C2.18	$SO_4^{\bullet-} + Mn^{2+} \rightarrow Mn^{3+} + SO_4^{2-}$	$1.4 \times 10^7 (E_a = 34)$	20 °C, pH 3–5	[52]
		2.0×10^7		[270]
C2.19	$[Mn^{II}(SO_4^{\bullet})]^- \rightarrow Mn^{3+} + SO_4^{2-}$	$k_{ET} = 2.6 \times 10^6$	20 °C, pH 3–5	[52]
C2.20	$SO_4^{\bullet-} + Ti^{2+} \rightarrow Ti^{3+} + SO_4^{2-}$	1.7×10^9		[270]
C2.21	$SO_4^{\bullet-} + Ag^+ \rightarrow Ag^{2+} + SO_4^{2-}$	1.8×10^9		[270]
C2.22	$SO_4^{\bullet-} + Co^{2+} \rightarrow Co^{3+} + SO_4^{2-}$	2.0×10^6		[270]
C2.23	$SO_4^{\bullet-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\bullet}$	2×10^8		[270]
		3.0×10^8	$I = 0\,M$	[335]
		3.1×10^8	$pH \sim 6.0$	[276]
		$3.0 \times 10^8 (E_a = 0)$	~25°C, $I = 0\,M$	[340]
C2.24	$SO_4^{\bullet-} + Br^- \rightarrow SO_4^{2-} + Br^{\bullet}$	2.1×10^9		[341]
		3.5×10^9		[270]
C2.25	$SO_4^{\bullet-} + N_3^- \rightarrow SO_4^{2-} + N_3^{\bullet}$	$2.4 \times 10^9 (E_a = 10)$	25 °C, $I = 0\,M$	[340]
C2.26	$SO_4^{\bullet-} + HCO_3^- \rightarrow SO_4^{2-} + CO_3^{2-} + H^+$	$2.8 \times 10^6 (E_a = 17)$	23 °C, $I = 0\,M$	[340]
C2.27	$SO_4^{\bullet-} + CO_3^{2-} \rightarrow SO_4^{2-} + CO_3^{2-}$	4.1×10^7		[69]
C2.28	$SO_4^{\bullet-} + HCOOH(+O_2) \rightarrow SO_4^{2-} + H^+ + HO_2^{\bullet} + CO_2$	2.5×10^6		[331]
C2.29	$SO_4^{\bullet-} + HCOO^-(+O_2) \rightarrow SO_4^{2-} + HO_2^{\bullet} + CO_2$	2.1×10^7		[331]
C2.30	$SO_4^{\bullet-} + CH_3OH(+O_2) \rightarrow SO_4^{2-} + H^+ + HO_2^{\bullet} + CH_3CHO$	$9.0 \times 10^6 (E_a = 18)$		[342]
C2.31	$SO_4^{\bullet-} + CH_3CH_2OH(+O_2) \rightarrow SO_4^{2-} + H^+ + HO_2^{\bullet} + HCHO$	$4.1 \times 10^7 (E_a = 15)$		[342]
C2.32	$SO_4^{\bullet-} + CH_2(OH)_2(+O_2) \rightarrow SO_4^{2-} + H^+ + HO_2^{\bullet} + HCOOH$	$1.4 \times 10^7 (E_a = 11)$		[381]
C2.33	$SO_4^{\bullet-} + CH_3COOH(+O_2) \rightarrow SO_4^{2-} + H^+ + CH_3O_2 + CO_2$	2.0×10^5		[69, 331]

(*continued*)

No.	Elementary reaction	k ($M^{-1}\,s^{-1}$); (E_a in kJ mol^{-1})	Condition	Reference
C2.34	$SO_4^{\bullet-} + CH_3COO^- (+O_2) \rightarrow SO_4^{2-} + CH_3O_2 + CO_2$	3.7×10^6	25 °C, I = 0 M	[330]
		3.9×10^6	25 °C, I = 0 M	[340]
		5.0×10^6		[276]
		2.8×10^7 ($E_a = 10$)		[331]
C2.35	$SO_5^{\bullet-} + HO_2^{\bullet} \rightarrow +HSO_5^- + O_2$	5.5×10^7		[272]
		1.7×10^9		[324]
C2.36	$SO_5^{\bullet-} + O_2^{\bullet-} (+H_2O) \rightarrow +HSO_5^- + HO^- + O_2$	1.9×10^7		[38]
C2.37	$SO_5^{\bullet-} + O_2^{\bullet-} (+H^+) \rightarrow +HSO_5^- + O_2$	2.3×10^8		[185]
		2.3×10^7		[144]
C2.38	$SO_5^{\bullet-} + HSO_3^- \rightarrow +HSO_5^- + SO_3^{\bullet-} \rightarrow H^+ + SO_4^{2-} + SO_4^{\bullet-}$	3.6×10^3		[272]
C2.39	$SO_5^{\bullet-} + HSO_3^- \rightarrow +HSO_5^- + SO_3^{\bullet-}$	8.5×10^3		[144]
		8.6×10^3		[185]
		2.5×10^4	pH 4.9	[327]
		7.5×10^4		[332]
		$<3.0 \times 10^5$		[327]
		3.0×10^6	pH 6.8	[58]
		1.3×10^7	pH 8.7	[327]
C2.40	$SO_5^{\bullet-} + SO_3^{2-} (+H^+) \rightarrow +HSO_5^- + SO_3^{\bullet-}$	2.1×10^5	acidic	[185]
		3.0×10^6		[38]
		3.8×10^6		[332]
C2.41	$SO_5^{\bullet-} + SO_3^{2-} \rightarrow SO_5^{2-} + SO_3^{\bullet-}$	3.6×10^5	pH 9	[185]
C2.42	$SO_5^{\bullet-} + HSO_3^- \rightarrow +HSO_4^- + SO_4^{\bullet-}$ (or $SO_5^{\bullet-} + HSO_3^- \rightarrow H^+ + SO_4^{2-} + SO_4^{\bullet-}$)	3.6×10^2		[185]
		2.5×10^4	pH 4.9	[332]
		$<3.0 \times 10^5$		[327]
		1.3×10^7		[67]
		3.0×10^8		[144]
C2.43	$SO_5^{\bullet-} + SO_3^{2-} \rightarrow SO_4^{2-} + SO_4^{\bullet-}$	1.3×10^5		[163]
		1.4×10^5	pH 9	[185]
C2.44	$SO_5^{\bullet-} + SO_3^{2-} (+H^+) \rightarrow +HSO_4^- + SO_4^{\bullet-}$	7.5×10^4		[327]
		5.5×10^6		[185]
		9.0×10^6		[332]
		1.0×10^7		[38]
C2.45	$SO_5^{\bullet-} + Fe^{2+} \rightarrow FeOH^{2+} + HSO_5^-$	$0.6 - 3 \times 10^6$		[343]
C2.46	$HSO_5^- + HO^{\bullet} \rightarrow SO_5^{\bullet-} + H_2O$	1.7×10^7	pH 7.0	[217]
C2.47	$HSO_5^- + Cl_2^{\bullet-} \rightarrow 2Cl^- + H^+ + SO_5^{\bullet-}$	$<1.0 \times 10^5$		[54]
C2.48	$SO_5^{2-} + Cl_2^{\bullet-} \rightarrow 2Cl^- + SO_5^{\bullet-}$	1.0×10^8		[54]
C2.49	$HSO_5^- + HSO_3^- \rightarrow 2SO_4^{2-} + 2H^+$	$\sim 1 \times 10^3$		[144]
C2.50	$HSO_5^- + HSO_3^- + H^+ \rightarrow 2 + HSO_4^- + H^+$	5.6×10^6		[217]
C2.51	$HSO_3^- + HSO_5^- \rightarrow 2 + HSO_4^-$	3.5×10^2	pH 8.0	[38]
		9.1×10^3	pH 2.9	[217]
		2.0×10^4	pH 2.5	[217]
		7.9×10^4	pH 1.5	[217]
		7.5×10^5		[12]
		7.1×10^6 ($E_a = 26$)	5 °C, I = 0.2 M	[217]
		$1 + [H^+]10^7$		[54]
C2.52	$HSO_5^- + Fe^{2+} \rightarrow FeOH^{2+} + SO_4^{\bullet-}$	3×10^4		[343]
C2.53	$HSO_5^- + \Delta \rightarrow OH^{\bullet} + SO_4^{\bullet-}$	$4.9 \times 10^{-9}\,s^{-1}$		[215]

C3 *Rate constants for elementary reactons involving radical recombination*

No.	Elementary reaction	k (M^{-1} s^{-1}); (E_a in kJ mol^{-1})	Condition	Reference
C3.1	$2SO_3^{\bullet -} \rightarrow S_2O_6^{2-}$	1.6×10^8 ($E_a = 10.3$)	I = 0 M,	[185, 324]
		2.4×10^8		[335]
		$1.8\text{–}4.3 \times 10^8$	I = 0 M	[56, 152]
		1.8×10^8	pH:4–5, T = 25°C	[56]
		4.8×10^8	T = 20°C	[269]
		5.0×10^8		[185]
C3.2	$2SO_3^{\bullet -} \rightarrow SO_3 + SO_3^{2-}$	2.3×10^8	T = 25°C, pH 4.3	[56]
		3.2×10^8	I = 0 M	[335]
		6.8×10^8	pH 9.8	[344]
		7.2×10^8	pH 10.7	[345]
		8.5×10^8	pH 5.0	[152]
		1.1×10^9	pH 9.8	[55]
		1.4×10^9	pH 10.0	[152]
		1.6×10^9	pH 14.0	[346]
		1.9×10^9	pH 11.8	[347]
C3.3	$2SO_4^{\bullet -} \rightarrow S_2O_8^{2-}$	1.6×10^8		[338]
		2.3×10^8		[325]
		4.1×10^8	I = 0 M	[185]
		7.0×10^8		[54]
C3.4	$2SO_4^{\bullet -} \rightarrow$ products	3.7×10^8	25 °C pH 0.1–4.8	[193]
		4.2×10^8	25 °C pH 5.5	[260]
C3.5	$2SO_5^{\bullet -} \rightarrow 2SO_4^{\bullet -} + O_2$	6.0×10^4		[144]
		7.2×10^6 (Ea = 22)		[338]
		8.4×10^6		[332]
		8.7×10^7		[271]
		1.0×10^8		[330]
		2.0×10^8		[348]
		2.1×10^8		[54]
		2.2×10^8		[185]
		3.0×10^8		[327]
		6.0×10^8		[349]
C3.6	$2SO_5^{\bullet -} \rightarrow S_2O_8^{2-} + O_2^{(*)}$	1.4×10^7		[271]
		4.8×10^7	I = 0 M	[185]
		9.3×10^7		[144]
		1.3×10^8		[69]
		1.4×10^8		[349]
		1.8×10^8 (Ea = 22)		[338]
		2.2×10^8		[54]

C4 *Rate constants for elementary reactons involving Fe(II) oxidation*

No.	Elementary reaction	k (M^{-1} s^{-1}); (E_a in kJ mol^{-1})	Condition	Reference
C4.1	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$	5.2×10^1 (Ea = 42)	20 °C, 5–300 °C	[263]
		6.0×10^1	pH 0.4–2	[265]
		6.3×10^1	25 °C, pH 4.5	[264]
C4.2	$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$	2.3×10^8	pH 1.0	[350]
		3.2×10^8	pH 7.0	[351]
		4.3×10^8		[351]
		4.3×10^8 ($E_a = 9.1$)	pH 3.0	[99]
C4.3	$Fe^{2+} + {}^{\bullet}HO_2 + (H^+) \rightarrow Fe^{3+} + H_2O_2$	1.2×10^6 ($E_a = 42$)		[262]
C4.4	$Fe^{2+} + O_2^{\bullet-} + (2H^+) \rightarrow Fe^{3+} + H_2O_2$	1.0×10^7		[265]
C4.5	$Fe^{2+} + SO_3^{\bullet-} \leftrightarrow [Fe^{II}S^{V}O_3^{\bullet}]^-$	$K = 280^{\&}$	pH 4	[53]
C4.6	$[Fe^{II}S^{V}O_3^{\bullet}]^- \rightarrow Fe^{3+} + SO_3^{2-}$	$k_{ET} = 3.1 \times 10^4\ s^{-1}$	pH 4	[53]
C4.7	$Fe^{2+} + SO_3^{\bullet-} \rightarrow Fe^{3+} + SO_3$	9.8×10^6	pH 4	[114]
C4.8	$Fe^{2+} + SO_4^{\bullet-} \leftrightarrow [Fe^{II}(S^{VII}O_4^{\bullet})]^-$	$K = 5.3$	20 °C, pH 3–5	[52]
C4.9	$[Fe^{II}(S^{VII}O_4^{\bullet})]^- \rightarrow Fe^{III} + SO_4^{2-}$	$k_{ET} = 1.1 \times 10^9\ s^{-1}$	20 °C, pH 3–5	[52]
C4.10	$Fe^{2+} + SO_4^{\bullet-} \rightarrow FeSO_4^+$	4.0×10^7	pH 2.1	[325]
		8.6×10^8		[352]
		9.9×10^8		[353]
C4.11	$Fe^{2+} + SO_4^{\bullet-} \rightarrow Fe^{3+} + SO_4^{2-}$	$k = 4.6 \times 10^9$ ($E_a = -18$)	20 °C, pH 3–5	[52]
C4.12	$Fe^{2+} + SO_4^{\bullet-}(+H_2O)$	3.5×10^7		[214]
	$\rightarrow FeOH^{2+} + SO_4^{2-} + H^+$	4.1×10^7		[325]
C4.13	$Fe^{2+} + SO_5^{\bullet-}(+H_2O) \rightarrow FeOH^{2+} + HSO_5^-$	$0.6–3 \times 10^6$		[343]
		4.3×10^7		[354]
C4.14	$Fe^{2+} + SO_5^{\bullet-} \rightarrow Fe^{3+} + SO_5^{2-}$	3.2×10^6		[215]*
		4.3×10^7	pH 4.5	[354]
C4.15	$Fe^{2+} + SO_5^{\bullet-} + H^+ \rightarrow Fe^{3+} + HSO_5^{2-}$	4.3×10^7		[354]
		2.0×10^8		[114]
C4.16	$Fe^{2+} + HSO_5^- \rightarrow FeOH^{2+} + SO_4^{\bullet-}$	3×10^4		[214]
C4.17	$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + SO_4^{2-} + {}^{\bullet}OH$	3×10^4		[355]
C4.18	$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet-}$	$(1.2 \times 10^1 + 5.5 \times 10^1[H^+])$ ($E_a = 62$)	30 °C, I = 1.0 M, $0.4 < [H^+] < 1$ M	[294]
		2×10^1	22 °C	[163]
		2.7×10^1		[356]
		1.0×10^2		[141]
C4.19	$Fe^{2+} + S_2O_8^{2-}(+H_2O) \rightarrow$	1.7×10^1		[52]
C4.20	$FeOH^{2+} + SO_4^{2-} + SO_4^{\bullet-} + H^+$			
C4.21	$Fe^{2+} + HS_2O_8^- \rightarrow Fe^{3+} + HSO_4^- + SO_4^{\bullet-}$	$>1.3 \times 10^3$($E_a = 32$)	35 °C, I = 1.0 M	[294]
C4.22	$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$	3.1×10^4	pH < 0.4	[53]
C4.23	$Fe^{II}SO_3 + SO_3^{\bullet-} \rightarrow Fe^{3+} + 2SO_3^{2-}$	3.2×10^6		[304]

(*continued*)

No.	Elementary reaction	k ($M^{-1}\,s^{-1}$); (E_a in kJ mol^{-1})	Condition	Reference
C4.24	$Fe^{2+} + Mn^{3+} \rightarrow Fe^{3+} + Mn^{2+}$	1.5×10^4		[357]
C4.25	$Fe^{2+} + Cl_2^{\bullet -} \rightarrow 2Cl^- + Fe^{3+}$	1.0×10^7 ($E_a = 25$)		[358]
C4.26	$Fe^{2+} + Br_2^{\bullet -} \rightarrow 2Br^- + Fe^{3+}$	3.6×10^6 ($E_a = 28$)		[358]
C4.27	$Fe^{2+} + CO_3^{\bullet -} \rightarrow CO_3^{2-} + Fe^{3+}$	Est 2×10^7		[69]
C4.28	$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2$	8.2×10^5	25 °C, pH 0–2, I = 0–1 M	[359]
C4.29	$FeO^{2+} + Fe^{2+} + (2H^+) \rightarrow 2Fe^{3+} + H_2O$	1.4×10^5	25 °C, pH 0–2, I = 0–1 M	[359]
C4.30	$FeO^{2+} + (H^+) \rightarrow Fe^{3+} + \frac{1}{2}{}^{\bullet}OH + \frac{1}{2}OH^-$	$1.3 \times 10^{-2}\,s^{-1}$	25 °C, pH 0–2, I = 0–1 M	[359]
C4.31	$FeO^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + HO_2^{\bullet -}$	1.0×10^7	25 °C, pH 0–2, I = 0–1 M	[359]
C4.32	$FeO^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO_2^{\bullet} + OH^-$	1.0×10^4	25 °C, pH 0–2, I = 0–1 M	[359]
C4.33	$FeO^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{\bullet} + OH^-$	2.0×10^6	25 °C, pH 0–2, I = 0–1 M	[359]
C4.34	$Fe^{II}L + HSO_5^- \rightarrow Fe^{III}L + SO_4^{\bullet -} + OH^-$ (where L = EDTA/NTA/DTPA)	~3×10^4	25 °C, pH ~ 2	[201]

C5 *Rate constants for elementary reactons involving Fe(III) reduction*

No.	Elementary reaction	k ($M^{-1}\,s^{-1}$); (E_a in kJ mol^{-1})	Condition	Reference
C5.1	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$	2×10^{-3}		[266, 267]
C5.2	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OH + OH^-$	7.6×10^1		[218]
C5.3	$Fe^{3+} + O_2^{\bullet -} \rightarrow Fe^{2+} + O_2$	1.5×10^8		[265]
C5.4	$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+$	$<1.0 \times 10^4$		[265]
C5.5	$Fe^{III}OH^{2+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H_2O$	1.3×10^5		[214]
C5.6	$Fe^{III}OH^{2+} + O_2^{\bullet -} \rightarrow Fe^{2+} + OH^- + O_2$	1.5×10^8		[215]*
C5.7	$Fe^{III}(OH)_2^+ + O_2^{\bullet -} \rightarrow Fe^{2+} + 2OH^- + O_2$	1.5×10^8		[215]*
C5.8	$Fe^{III}OH^{2+} + HSO_3^- \rightarrow Fe^{2+} + SO_3^{\bullet -} + H_2O$	3.9×10^1		[214]
C5.9	$Fe^{3+} + SO_3^{\bullet -}(+H_2O) \rightarrow Fe^{2+} + SO_4^{2-} + H^+$	1.5×10^7		[114]
C5.10	$Fe^{III}SO_3^+ \rightarrow Fe^{2+} + SO_3^{\bullet -}$	$2.1 \times 10^{-3}\,s^{-1}$	pH 2.0	[136]
		$1.4 \times 10^{-1}\,s^{-1}$	pH 2.5	[73]
		$1.9 \times 10^{-1}\,s^{-1}$	25 °C, I = 1.0 M	[45]
		$2 \times 10^{-1}\,s^{-1}$	pH 2.5	[114]
C5.11	**$Fe^{III}O + HSO_3H^+(+O_2) \rightarrow Fe^{2+} + H_2O + SO_5^{\bullet -}$	$6.5 \times 10^{-2}\,s^{-1}$		[214]
	$(Fe^{III}O + HSO_3H^+ \rightarrow Fe^{2+} + H_2O + SO_3^{\bullet -})$	$2 \times 10^{-1}\,s^{-1}$		[141]
C5.12	$Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+}$	3×10^7		[360]
C5.13	$[HOFe^{III}OS^{IV}O_2] \leftrightarrow [HOFe^{II}OS^{V}O_2]$	$4 \times 10^{-2}\,s^{-1}$	25 °C, I = 0.4 M, pH 2.1	[136]

*Quoted in Yermakov *et al.* 2003 [215], but original source unclear.

**Expression in Yermakov *et al.* 2003 [215] as $Fe^{III}OHSO_3H^+(+O_2) \rightarrow Fe^{2+} + H_2O + SO_5^{\bullet -}$, with rate given in unit s^{-1}. If molecular oxygen is required in the decay, then $0.2\,s^{-1}$ represent the rate constant at O_2-abundant condition. It is possible that the complex first decomposes to give $SO_3^{\bullet -}$, which then reacts with O_2 to give $SO_5^{\bullet -}$.

C6 *Rate constants for elementary photolysis reactions*

No.	Elementary reaction	k(s^{-1})	Reference
C6.1	$Fe^{III}OH^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$	4.5×10^{-3}	[254]
C6.2	$Fe^{III}(OH)_2^+ + h\nu \rightarrow Fe^{2+} + OH^- + {}^{\bullet}OH$	5.8×10^{-3}	[361]
C6.3	$Fe^{III}SO_4^+ + h\nu \rightarrow Fe^{2+} + SO_4^{\bullet-}$	6.4×10^{-3}	[254]
C6.4	$HSO_3^- + h\nu \rightarrow H^+ + SO_3^{\bullet-}$	2.9×10^{-5}	[144]
C6.5	$SO_3^{2-} + h\nu \rightarrow SO_3^{\bullet-} + e_{aq}^-$	6.0×10^{-5}	[144]
C6.6	$SO_4^{2-} + h\nu(\lambda_{exc} < 200\,nm) \rightarrow SO_4^{\bullet-}$	–	[260]
C6.7	$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH$	7.2×10^{-6}	[362]
C6.8	$NO_2^- + h\nu(+H^+) \rightarrow NO + {}^{\bullet}OH$	2.6×10^{-5}	[362]
C6.9	$NO_2^- + hv(+H_2O) \rightarrow NO + {}^{\bullet}OH + OH^-$	2.6×10^{-5}	[215]*
C6.10	$NO_3^- + h\nu(+H^+) \rightarrow NO_2 + {}^{\bullet}OH$	4.3×10^{-7}	[362]
C6.11	$NO_3^- + hv(+H_2O) \rightarrow NO_2 + {}^{\bullet}OH + OH^-$	5.6×10^{-5}	[215]*

*Quoted in Yermakov *et al.* 2003 [215], but original source unclear.

C7 *Rate constants for other elementary reactions related to aque. Fe-S(IV)-O_2 system*

No.	Elementary reaction	k($M^{-1}s^{-1}$); ($E_a$in kJ mol^{-1})	Condition	Reference
C7.1	$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$	7.5×10^9		[144]
		2×10^{10}		[296]
		2.1×10^{10}		[261]
C7.2	$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet}$	5.0×10^{10}		[296]
C7.3	$O_2^{\bullet-} + O_3(+H^+) \rightarrow 2O_2 + {}^{\bullet}OH$	1.5×10^9		[363]
C7.4	$O_2^{\bullet-} + {}^{\bullet}OH \rightarrow O_2 + OH^-$	$1.1 \times 10^{10}(E_a = 18)$		[364]
C7.5	$O_2^{\bullet-} \rightarrow$ products	$1.9 \times 10^2 s^{-1}$		[185]
C7.6	$HO_2^{\bullet} + OH^{\bullet} \rightarrow H_2O + O_2$	1.0×10^{10}		[365]
C7.7	$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$	$8.3 \times 10^5(E_a = 23)$		[296]
C7.8	$HO_2^{\bullet} + O_2^{\bullet-}(+H^+) \rightarrow H_2O_2 + O_2$	9.7×10^8		[144]
C7.9	$HO_2^{\bullet} + O_2 + H_2O \rightarrow H_2O_2 + O_2 + OH^-$	$9.7 \times 10^7(E_a = 8.8)$		[296]
C7.10	$HO_2^{\bullet} \rightarrow H^+ + O_2^{\bullet-}$	$6.5 \times 10^5\,s^{-1}$		[296]
C7.11	$HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2$	1.1×10^5		[299]
C7.12	${}^{\bullet}OH + HSO_4^- \rightarrow H_2O + SO_4^{\bullet-}$	3.5×10^5		[366]
C7.13	${}^{\bullet}OH + HSO_5^- \rightarrow H_2O + SO_5^{\bullet-}$	5.0×10^6		[54]
C7.14	${}^{\bullet}OH + SO_5^{2-} \rightarrow OH^- + SO_5^{\bullet-}$	2.1×10^9		[367]
C7.15	${}^{\bullet}OH + S_2O_8^{2-} \rightarrow OH^- + S_2O_8^{\bullet-}$	1.2×10^7		[54]
C7.16	$O_3^- + H^+ \rightarrow HO_3^{\bullet}$	5.5×10^{10}		[299]
C7.17	$O_3^- + H_2O \rightarrow HO_3^{\bullet} + OH^-$	8.5×10^9		[299]
C7.18	$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet}$	$2.7 \times 10^7(E_a = 14)$	25 °C, pH 7–14	[368]
C7.19	$S_2O_7^{2-} + H_2O \rightarrow 2SO_4^{2-} + 2H^+$	1.3×10^{-2}	25 °C, pH 2–5, $I = 0.5\,M$	[216]
C7.20	$S_2O_8^{2-}(+H_2O) \rightarrow 2SO_4^{\bullet-}$	$1.1 \times 10^{-8}\,s^{-1}$		[178]
		$1.0 \times 10^{-7}\,s^{-1}$	25 °C, pH 1.3	[274]
		$5.7 \times 10^{-5}\,s^{-1}$	70 °C, pH 1.3	[274]

(*continued*)

No.	Elementary reaction	$k(M^{-1}s^{-1})$; (E_a in kJ mol^{-1})	Condition	Reference
C7.21	$S_2O_8^{2-} + Ag^+ \rightarrow 2SO_4^{\bullet -} + Ag^+$	$3.3 \times 10^{-3} - 2.2 \times 10^{-2}$	25 °C	[274]
C7.22	$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet -}$	2.1×10^{10}		[262]
C7.23	$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$	7.4×10^7	25 °C	[333]
		1.6×10^7	55 °C	[12]
C7.24	$e_{aq}^- + O_2 \rightarrow O_2^{\bullet -}$	1.9×10^{10}		[261]
		2.0×10^{10}		[296]
C7.25	$e_{aq}^- + N_2O \rightarrow N_2 + OH^{\cdot} + OH^-$	9.1×10^9		[261]
C7.26	$e_{aq}^- + H^+ \rightarrow H^{\bullet}$	2.3×10^{10}		[261]

*Quoted in Yermakov *et al.* 2003 [215], but original source unclear.

C8 *Forward (k_{for}) and backward (k_{bk}) rate constants for selected reactions at 25 °C**

No.	Reaction	$k_{for}(s^{-1})$ (E_a in kJ mol^{-1})	$k_{bk}(M^{-1}\,s^{-1})$	log K**	log K_{Lit}^c
C8.1	$H_2O \leftrightarrow H^+ + OH^-$	2.3×10^{-5} (Ea = 57) [369]	1.3×10^{11} [370]	−15.7	−14.0 [292]
C8.2	$2Fe^{3+}(+2H_2O) \leftrightarrow Fe_2(OH)_2^{4+} + 2H^+$	3.6×10^{-3a} [138]	6.7×10^{3b} [138]	−6.3	−2.9
C8.3	$Fe^{3+}(+2H_2O) \leftrightarrow Fe(OH)_2^+ + 2H^+$	3.5×10^0 [138]	2.5×10^0 [138]	1.5	−5.8
C8.4	$Fe_2(OH)SO_4^{3+} \leftrightarrow FeOH^{2+} + FeSO_4^+$	4.6×10^0 [47]	2.0×10^2 [47]	−1.6	–[e]
C8.5	$HSO_5^- \leftrightarrow H^+ + SO_5^{2-}$	2.0×10^1 [185, 371]	5×10^{10} [371]	−9.4	−9.6
C8.6	$2HSO_3^- \leftrightarrow S_2O_5^{2-} + H_2O$	7×10^{2a} [96]	1×10^{4b} [96]	−1.2	−1.2
C8.7	$FeOH^{2+} + H_2O \leftrightarrow Fe(OH)_2^+ + H^+$	1.1×10^{3a} [372]	8.0×10^9 [372]	−6.9	−3.6[d]
		6.1×10^{4a} [372]		−5.1	
		5.6×10^{5a} [215]		−4.2	
C8.8	$HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$	3.1×10^3 ($E_a = -16$) [373]	5×10^{10} [370]	−7.2	−7.2
C8.9	$Fe^{3+} + SO_4^{2-} \leftrightarrow FeSO_4^+$	(I~0.5 M)4.7×10^{3a} [26]	1.8×10^{5b} [26]	−1.6	4.2[d]
C8.10	$Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+$	$4.7 \times 10^{4a\,[26]}$	4.3×10^8 [26]	−4.0	−2.2[d]
C8.11	$SO_2 + H_2O \leftrightarrow H^+ + HSO_3^-$	6.3×10^{4a} ($E_a = -16$) [373]	2.0×10^8 [370]	−3.5	−1.9
		1.0×10^{8a} [374]	2.5×10^9 [374]	−1.4[f]	
C8.12	$Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+$	8.6×10^{5a} [215]	4.3×10^8 [215]	−2.7	−2.2
			1.5×10^9 [99]	−3.2	
		3.5×10^{-1a} [138]	1.3×10^2 [138]	−2.6	
C8.13	$CH_3COOH \leftrightarrow H^+ + CH_3COO^-$	8.8×10^5 ($E_a = 0$)[369]	5×10^{10} [370]	−4.8	−4.8
C8.14	$Fe^{3+} + SO_4^{2-} \leftrightarrow FeSO_4^+$	3.2×10^{7a} [215]	1.8×10^{5b} [215]	2.3	4.2
C8.15	$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$	1.0×10^9 ($E_a = -22$) [375]	1×10^{11} [370]	−2.0	−2.0
C8.16	$Fe^{3+} + HSO_3^- \leftrightarrow FeHSO_3^{2+}$	5.0×10^{10a} [215]	6.9×10^{8b} [215]	1.9	1.8
C8.17	$FeOH^{2+} + HSO_3^- \leftrightarrow FeOHSO_3H^+$	5.0×10^{10a} [215]	8.3×10^{7b} [215]	2.8	2.8
C8.18	$Fe^{3+} + SO_3^{2-} \leftrightarrow FeSO_3^+$	5.0×10^{10a} [215]	6.9×10^{3b} [215]	6.9	2.0

(*continued*)

No.	Reaction	$k_{for}(s^{-1})$ (E_a in $kJmol^{-1}$)	$k_{bk}(M^{-1}s^{-1})$	log K**	log K^c_{Lit}
C8.19	$FeOH^{2+} + SO_3^{2-} \leftrightarrow FeOHSO_3$	5.0×10^{10a} [215]	2.5×10^{3b} [215]	7.3	8.6
C8.20	$HNO_3 \leftrightarrow H^+ + NO_3^-$	$1.1 \times 10^{12}(E_a = -15)$ [375]	5×10^{10} [370]	1.3	1.4
C8.21	$H_2SO_4 \leftrightarrow H^+ + HSO_4^-$	5.0×10^{12} [215]	5.0×10^{10} [215]	2.0	–[e]
C8.22	$Fe^{2+} + SO_4^{2-} \leftrightarrow FeSO_4$	7.9×10^{12a} [215]	5.0×10^{10b} [215]	2.2	2.3
C8.23	$HCl \leftrightarrow H^+ + Cl^-$	$8.6 \times 10^{16}(E_a = -57)$ [376]	5×10^{10} [370]	−6.2	−6.2 [376]

*Original reference unclear for rate constants quoted from Yermakov *et al.* 2003 [215].
**Where $K = k_{for}/k_{bk}$.
[a] Second order k_{for} in unit M^{-1} s^{-1}.
[b] First order k_{bk} in unit s^{-1}.
[c] $K_{Lit} = K_{eqm}$ reported in literature. Values from **B1**, **B2**, **B3**, and **B5**.
[d] Calculated from average of the values reported in **B3** and **B5** and acid dissociation constant for H_2O.
[e] Not found.
[f] At ionic strength of 0.9 M.

C9 *Rate expression for catalytic and non-catalytic oxidation of S(IV) and Fe(II)*

Rate expression*	Condition	Reference
Non-catalytic S(IV) oxidation		
$r_{S(IV)} = 2r_{O2} = 2\,k[HSO_3^-]^2[H^+]^{-2}$	25 °C, I = 0.05 M, pH ~4–6	[216]
$k = 3.6 \times 10^6\ s^{-1}$		
$r_{S(IV)} = k[S^{IV}]$	30 °C, I = 0.1–1.0 M	[377]
$k = 4.5 \times 10^{-5}\ s^{-1}$		
$r_{S(IV)} = k_I[S(IV)]^2[O_2]^{1/2}$	15–45 °C, pH 4–8.5, salinity ~3.5%	[164]
$\ln k_I = 19.5 - 5070/T + 14.7I^{1/2} - 2.9I - 2880I^{1/2}$;		
(k_I in $M^{-1.5}\ min^{-1}$); $E_a = 140\ kJ\ mol^{-1}$		
$r_{S(IV)} = k[S(IV)][H^+]^{-0.7}$	10–30 °C, pH 2–6	[283]
$k = 1.2 \times 10^{-5}\ M^{0.7}\ s^{-1}$; $E_a = 30\ kJ\ mol^{-1}$	seawater	
Non-catalytic Fe(II) oxidation		
$r_{Fe(II)} = k_1[Fe^{2+}][OH^-]^2P_{O2}$	25 °C, pH > 4.5	[378]
$r_{Fe(II)} = k_2[Fe^{2+}]P_{O2}$	25 °C, pH < 4.5	
$k_1 = 1.3 \times 10^{12}\ M^{-2}atm^{-1}\ s^{-1}$		
$k_2 = 1.7 \times 10^{-9}\ atm^{-1}\ s^{-1}$		
$r_{Fe(II)} = k_I[Fe(II)][O_2][OH^-]^2$	5–45 °C, pH 5–9,	[158]
$\ln k_I = 21.6 - 1550/T + 3.3I^{1/2} - 1.5I$	salinity 0–3.5%	
(k_I in $M^{-3}\ min^{-1}$); $E_a = 29\ kJ\ mol^{-1}$		
Catalytic S(IV) oxidation		
$r_{S(IV)} = 6[Fe^{III}][S^{IV}]/[H^+]^*$	25 °C, pH 0–3	[67]
$r_{S(IV)} = 10^9[Fe^{III}]^2[S^{IV}]^*$	25 °C, pH 4	
$r_{S(IV)} = 10^{-3}[S^{IV}]^*$	25 °C, pH 5–6	

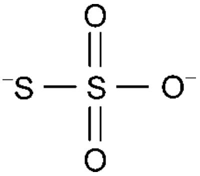
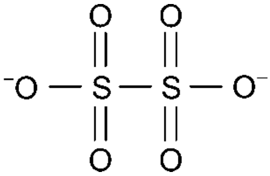
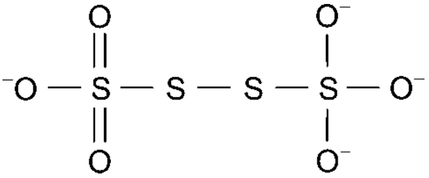
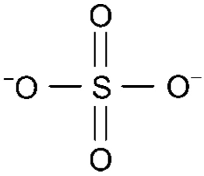
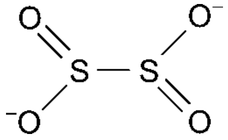
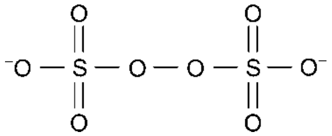
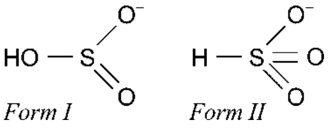
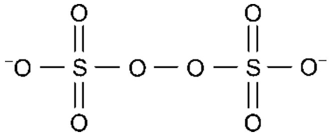
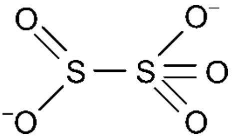
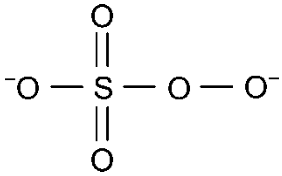
(*continued*)

Rate expression*	Condition	Reference
$r_{S(IV)} = 10^{-4}[S^{IV}]^*$	25 °C, pH 7	
$r_{S(IV)} = (k_1 + k_2[H^+]^{0.5} + k_3 P_{O2}[H^+]^{-1})[SO_3^{2-}]$	25 °C, pH 4–12, P_{O2} 0.11–1.0 atm	[379]
$k_1 = 4.4 \times 10^{-3}\,s^{-1}$		
$k_2 = 8.9\,M^{-0.5}\,s^{-1}$		
$k_3 = 3.9 \times 10^{-12} Matm^{-1}\,s^{-1}$		
$r_{S(IV)} = k[Fe(III)][S(IV)][H^+]^{-1}$	25 °C, pH 0–3	[64]
$k = 8.2 \times 10^{-1}\,s^{-1}$		
$r_{S(IV)} = k[Fe(III)][S(IV)][H^+]^{-1}$	20 °C, pH 4–5	[282][a]
$k = 1.0 \times 10^{-1}\,s^{-1}$		[136]
$r_{S(IV)} = k[Fe(III)][S(IV)][H^+]^{-1}$	20 °C, pH $\leq$ 4	[146][a]
$k = 7.6 \times 10^{-2}\,s^{-1}$		[136]
$r_{S(IV)} = k[Fe(III)][SO_3^{2-}]$	20 °C, pH 1.3–3.3	[145][a]
$k = 4.5 \times 10^5\,M^{-1}\,s^{-1}$		[136]
$r_{S(IV)} = k[Fe(III)][S(IV)]^2[H^+]^{-1}$	10 °C, pH 1.5–3.0	[380][a]
$k = 4.0 \times 10^1\,M^{-1}\,s^{-1}$		[136]
$r_{S(IV)} = k[Fe(III)][S(IV)]^2$	20 °C, pH $\geq$ 6	[146][a]
$k = 1.0 \times 10^5\,M^{-2}\,s^{-1}$		[136]
$r_{S(IV)} = k[Fe(III)][S(IV)]^2$	20 °C, pH $\geq$ 5	[282][a]
$k = 1.0 \times 10^7\,M^{-2}\,s^{-1}$		[136]
$r_{S(IV)} = k[Fe^{3+}][S(IV)]$	pH 4–8	[282]
$k = 1.0 \times 10^2\,M^{-1}\,s^{-1}$		
$r_{S(IV)} = k\alpha[Fe(III)][S(IV)]^2$	Compilation of all [a]studies	[136]
$k = 1.0\text{–}1.2 \times 10^6\,M^{-1}\,s^{-1}$		
$\alpha = K_{a1}K_{a2}/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$		
$-\log K_{a1} = 1.9$		
$-\log K_{a1} = 7.2$		
$r_{S(IV)} = k_I[Fe(II)]_o^{1.2}[HSO_3^-]^{0.6}[H^+]^{-1.1}[SO_4^{2-}]^{-0.4}$	25 °C, pH $\sim$0.7–2.3, $P_{O2} < 10$ bar	[98]
$\log k_I = 0.8\text{–}1 I^{1/2}[1 + I^{1/2}]^{-1}$		
$r_{S(IV)} = k[Fe^{3+}][HSO_3^-]^2[H^+]^{-1}$		[219]
$k = 2.6 \times 10^2\,M^{-1}\,s^{-1}$		
Catalytic Fe(II) oxidation		
$r_{Fe(II)} = k[S(IV)]^{1.40}[O_2]^{0.314}([Fe_T]/[SO_4^2]_i)^{1.06}/[H^+]_i^{0.062}$	25 °C	[74]
$r_{Fe(II)} = k[Fe^{2+}]^a[O_2]^b/[H_2SO_4]^c$	65–80 °C, 2% SO_2	[115]
$\{a \sim 2, b \sim 1, c \sim 0.25\text{–}0.35\}$		
$r_{Fe(II)} = k[Fe(III)][HSO_3^-]/[H^+]^{0.2}$	40–95 °C, 2% SO_2, pH: 0–3	[39]
Fe(III) reduction		
$r_{Fe(III)} = 0.004[Fe(III)][S(IV)][H^+]^{-2}(1 + 20[Fe^{2+}])$	25 °C, I = 1.0 M	[119]

*For atmospheric waters. Effects due to ionic strength, high S(IV), or the presence of organics can be empirically corrected. See Martin *et al.* 1991 [67], Kotronarou *et al.* 1993 [181].

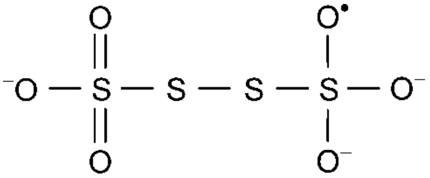
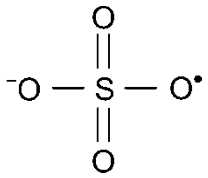
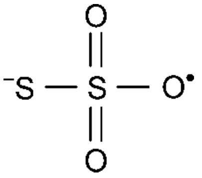
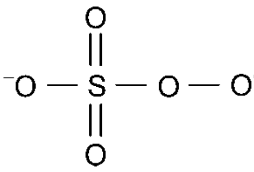
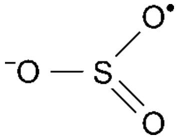
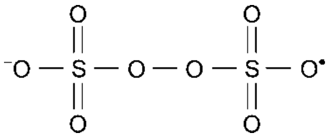
Appendix D: Molecular structures of oxysulphur anions and radicals

D1 *Structures of oxysulphur anions*

Oxidation state[a]	Molecular configuration	Oxidation state	Molecular configuration
S(II)	 Thiosulphate ($S_2O_3^{2-}$)[c]	S(V)[b]	 Dithionate ($S_2O_6^{2-}$)
S(II)	 Tetrathionate ($S_4O_6^{4-}$)[c]	S(VI)[b]	 Sulphate (SO_4^{2-})
S(III)[b]	 Dithionite/Hyposulphite ($S_2O_4^{4-}$)	S(VI)[b]	 Pyrosulphate ($S_2O_7^{2-}$)[f]
S(IV)[b]	 Bisulphite (HSO_3^-)[d]	S(VII)[b]	 Peroxydisulphate ($S_2O_8^{2-}$)[g]
S(IV)[b]	 Disulphite ($S_2O_5^{2-}$)[e]	S(VIII)[b]	 Peroxymonosulphate (SO_5^{2-})[g]

[a] Average oxidation state of sulphur atom.
[b] One of the several resonance stabilized configurations.
[c] Hypothesized structure based upon sulphur divalence and tetravalence. See the review on sulphur valence by Benson (1978) [382].
[d] Brandt and van Eldik (1995) [26].
[e] Brandt and van Eldik (1995) [26], Conklin and Hoffmann. (1988a) [44].
[f] Betterton and Hoffmann. (1988) [217], Connick *et al.* (1993) [216].
[g] Dogliotti *et al.* (1967) [193], Betterton and Hoffmann. (1988) [217].

D2 *Structures of oxysulphur radicals**

Oxidation state[a]	Molecular configuration	Oxidation state	Molecular configuration
S(IX/IV)	 Tetrathionate radical ($S_4O_6^{\bullet 3-}$)[c]	S(VII)	 Sulphate radical ($SO_4^{\bullet -}$)
S(V/II)	 Thiosulphate radical ($S_2O_3^{\bullet 3-}$)[b]	S(IX)	 Peroxymonosulphate radical ($SO_5^{\bullet -}$)
S(V)	 Sulphite radical ($SO_3^{\bullet -}$)	S(XV/II)	 Peroxydisulphate radical ($S_2O_8^{\bullet 3-}$)

[*] For convenience, the unpaired electron is drawn on the oxygen atom. In reality, the unpaired electron should reside on the S atom, stabilised by the resonance of electron densities from adjacent oxygen atoms.

[a] Averaged oxidation state of sulphur atom.

[b] Based on hypothesized structure.

[c] Postulated by Das *et al.* (1999) [57] in accordance to spectroscopic observation. A further rearrangement with an oxygen bridging into the sulphur backbone as suggested by the paper is not shown.