Oxidation of Cysteine and Glutathione by Soluble Polymeric MnO2

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The kinetics of reduction of soluble polymeric MnO2 by cysteine and glutathione has been studied in the pH range of 4.0–9.0. The concentration of thiols was varied between 1.0 and 2.0 mM, while the MnO2 concentration was varied between 2.0 and 12 μM. In this pH range, the reaction products were identified as Mn(II) and the corresponding disulfides (cystine and glutathione disulfide). Cystein or cysteinesulfonic acid was formed only when pH < 2. Experimental data indicate that the rate law over the pH range of 4–9 is first-order in both MnO2 and thiol concentration. Eyring plots for both thiols reacting with MnO2 indicate that the reaction is associative (∆Sat ~ −160 J mol−1 K−1) and proceeds via an inner-sphere redox process. The reaction proceeds via the formation of two different inner-sphere complexes =MnS2R− and =MnS2R and their further reaction to products. Both surface species are linked to each other via acid–base equilibria, and the rate constant decreases as pH increases. The presence of two ligand surface species is determined using surface complexation modeling. A reaction mechanism in agreement with the experimental results is proposed.

Introduction

Thiols are widespread in the environment. Many have been identified and quantified in a variety of samples from suboxic and anoxic waters and sediments, using electrochemical techniques (1–4) and/or chromatographic techniques (3, 5–9). Particularly in sediments, thiols are found in the nanomolar concentration range (2, 3, 5). Thiols are suspected to affect the bioavailability of essential trace metals (e.g., Cu and Zn) in sulfidic environments where they are strongly bound as solid sulfide minerals (3). Among the nonvolatile thiols reported in the literature, cysteine and glutathione are two of the most frequently found. Glutathione is a tripeptide formed by the amino acids glycine, cysteine, and glutamic acid and is thought to be the most abundant nonprotein thiol in animals, plants, and several bacteria (10, 11). Glutathione is a redox cofactor for proteins involving disulfide bonds (12, 13), works as a cysteine repository, and is possibly involved in the S0 metabolism (12). The main sources of cysteine, an essential amino acid for protein synthesis, are microbial protein degradation (14) and assimilatory sulfate reduction (15).

In aquatic environments, hydrogen sulfide can be readily oxidized by manganese and/or iron oxides, either biotically or abiotically, leading to the formation of several oxidized sulfur species such as sulfite, thiosulfate and polysulfides (16–21). Although the reductive dissolution of different iron oxides with several thiols has been studied in water (22–25), this is not the case for the manganese oxides.

To the best of our knowledge, the only report for this kind of reaction in the aqueous phase is included in the study of the reactivity of manganese(III/IV) oxides toward many different organic molecules done by Stone and Morgan (26). The authors used thiosalicylic acid as an example of a thiol and only reported an apparent second-order rate constant.

There are a few other reports in the literature for the reductive dissolution of manganese oxides with thiols in organic solvents (27–29) and with metallic oxides other than manganese and iron oxides, such as PbO2, CrO3, and Co2O3 (30). The study of the reductive dissolution of manganese oxides with thiols in water could contribute to a deeper and more complete knowledge of both the Mn and S biogeochemical cycles. Luther and Church (31) proposed that thiols could be oxidized to disulfides and even to sulfonic acids by reaction with manganese and iron oxides. Sulfonates have been confirmed in sediments in an XANES study (32). According to the results reported for the reaction of thiols with iron oxides in water, the only oxidation products are the corresponding disulfides (24, 25). The same products were reported in the oxidation with manganese oxides in organic solvents (27–29). In this work the study of the reductive dissolution of soluble polymeric manganese(IV) dioxide by cysteine and glutathione has been undertaken to find a rate law, identify the reaction products, and elucidate the elementary steps involved in this process over the pH range of 4.0–9.0.

Experimental Section

The soluble manganese dioxide used was a stable colloidal suspension, which we term polymeric. It was prepared following the technique described by Perez-Benito et al. (33) by mixing the appropriate amounts of KMnO4 (Aldrich) and Na2S2O3 (Aldrich) stock solutions, according to the following stoichiometry:

\[
3\text{S}_2\text{O}_3^{2-} + 8\text{MnO}_4^- + 2\text{H}^+ \rightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + \text{H}_2\text{O}
\]

Although this soluble phase is unlikely to exist in marine environments for extended periods, it is likely present in freshwater systems (34, 35). The polymeric manganese dioxide was electrochemically inactive (35) but showed a large absorption band covering the whole visible region of the spectrum with absorbance uniformly increasing with decreasing wavelength that gave a broad maximum at 300–400 nm (Figure 1). Dilutions of this polymeric oxide followed the Lambert–Beer law in the concentration range used (ε = 400 nm = 1.77 × 10^4 M−1 cm−1). The UV–Vis spectra were performed using a Hewlett-Packard 8453 diode array spectrophotometer.

The stoichiometry of the oxide was determined to be MnO2 (average of three replicates) by iodometric titrations using a Varian AA55 instrument for total Mn measurement. The point of zero charge (pzc) of the oxide was determined to be 1.93 by potentiometric titrations using a 716 Metrohm Titrisol equipped with a Metrohm pH glass combination electrode.
This polymeric phase is easy to synthesize, is stable for several months, is electrochemically inactive, and has been previously characterized (33). Some other properties of the polymeric oxide were previously reported (33, 36, 37): Negative particles roughly spherical, 90% of the particles had a diameter in the range of 89–193 nm, most of them had a diameter of 120 nm, and z-potential was $-47 \pm 3$ mV (33).

Thiol stock solutions were prepared fresh daily from the corresponding solids, cysteine (CSH) (Aldrich) and glutathione (GSH) (Merck), using degassed distilled deionized water (DDDW) and were standardized using Ellmann’s reagent (38). Oxidation-reduction experiments were performed under a nitrogen atmosphere. The temperature was held constant to $\pm 0.1$ °C with a constant temperature circulation bath. The pH was held constant between 4.0 and 9.0 using the appropriate buffer solutions (acetate, borate, and Tris). In all the experiments, the ionic strength was 0.02 M using NaClO4.

In one set of experiments designed to evaluate the influence of thiol concentration on the rate law, thiol concentration was varied between 1 and 2 mM, while MnO2 concentration was held constant. In another set of experiments, the MnO2 concentration was varied between 2 and 12 mM, while thiol concentration was held constant.

Under the experimental conditions used, the reaction was completed in less than 1 min. The course of the reaction was followed using a stopped-flow system coupled to a HP 8451 UV–Vis diode array spectrophotometer set to follow the decay in absorbance at 400 nm due to MnO2 consumption. The absorbance versus time data were fitted using the data analysis package included in the spectrophotometer software. The resulting rate constants for different experimental conditions are the average of at least three different runs.

Square-wave voltammetry (SWV) was used in separate experiments to evaluate the formation of Mn(II), Mn(III) (35, 39), and cysteine (cysteine sulfide) (1, 35) using an Analytical Instrument Systems, Inc. DLK 100 potentiostat with a EG&G PAR 303 static dropping mercury electrode stand (DME). The electrode stand was modified to use a saturated calomel electrode (SCE) rather than the Ag/AgCl reference supplied. The SCE electrode was connected to the solution through a NaCl salt bridge. Instrumental parameters for the SWV mode were typically 200 mV s$^{-1}$ scan rate over the potential range of $-0.1$ to 1.5 V with a 24-mV pulse height, which gave a detection limit lower than 1 $\mu$M. Because pyrophosphate forms stable complexes with Mn(III) at near neutral or slightly alkaline pH (39), separate electrochemical and spectrophotometric experiments were done in the presence of pyrophosphate (pH 8) in order to detect the formation of Mn(III).

Glutathione disulfide (GSSG) was identified and quantified according to the HPLC technique described by Winterbourn and Brennan (40) using a Shimadzu LC-6A instrument with a Shimadzu SPD-6AV UV–Vis detector. The samples were injected into a Rheodyne injector 7725i with a 50-$\mu$L loop and an i&j Scientific ACCU ODS 5-$\mu$m analytical chromatographic column. The retention time for GHS and GSSG under these operational conditions was 4.72 and 12.49 min, respectively. The analytical precision was usually within 1%.

In experiments performed below pH 2, cysteine was totally oxidized to an electrochemically inactive compound identified as cysteic (cysteinesulfonic) acid. The amount of cystic acid formed was evaluated by ion chromatography using a DIONEX DX-100 instrument with a conductivity detector, a sample injection valve, and a 25-$\mu$L sample loop. Two plastic anion columns were coupled in series to serve both as precolumn (DIONEX AG-9) and analytical chromatographic column (DIONEX AS-9). The suppressor was regenerated with 50 mM H2SO4 with a flow rate of 12.5 mL/min. A mixture of HCO3$^-$/CO3$^{2-}$ 4 mM was chosen as eluent with a flow rate of 1 mL/min. The retention time for cystic acid under these operational conditions was 3.92 min.

Standard cystine and cystic acid solutions were prepared by dissolving the corresponding amount of solid (used as received from Sigma) in DDW. Glutathione disulfide standards were prepared according to Luther et al. (1) by oxidizing a standardized solution of glutathione with I$_2$. Mn(III) standard solutions were prepared by diluting a 1000 ppm Mn(II) AAS standard (Fluka) in acidified distilled deionized water.

Errors for the k values were obtained from the fitting tool included in the HP8453 (diode array spectrophotometer) software package. Errors for the fitting parameters were obtained using the nonlinear curve fit tool in Microcal Origin software using the Levenberg–Marquardt fitting routine.

**Results and Discussion**

Experiments performed in the absence of thiols showed no change in the MnO2 UV–Vis spectra during the time scale of the kinetic experiments, indicating that there is no reaction of the MnO2 with the buffers used to keep pH constant. Similar results were obtained when cysteine was replaced by glycine, indicating that only the sulfhydryl group of cysteine is oxidized.

At a given pH value and thiol concentration, the initial rate is proportional to the amount of MnO2 added (Figure 2). At constant amount of manganese oxide added and pH, a linear correlation between the initial rate and the thiol concentration is observed (Figure 3). The experimental rate law is expressed as follows:

$$R_0 = k[\text{thiol}][\text{MnO}_2]_T$$

**FIGURE 1.** UV–Vis spectra of soluble polymeric MnO2.

**FIGURE 2.** Initial rate ($R_0$) of the reduction of MnO2 by thiols for different [MnO2] concentrations: cysteine (Δ) and glutathione (■), pH 4.1; $T = 25$ °C; $I = 0.02$ M, [thiol] = 1 mM.
The experiments, only the SH group is oxidized by MnO\textsubscript{2}.

Gluatamate, cysteine, and glycine. On the time scale used in glutathione is a tripeptide formed by the amino acids that for cysteine can be attributed to steric hindrance, since the fact that the reaction rate for glutathione is lower than

\textit{FIGURE 4. Rate constant for the reduction of MnO\textsubscript{2} by thiols at different pH values for cysteine (A) and glutathione (B); T = 25 °C; I = 0.02 M; [MnO\textsubscript{2}] = 20 \mu M.}

The dependence of k with temperature was in agreement with the Arrhenius equation (k = A e^(-Eh/RT)) where A is the preexponential factor, R is the gas constant, T is the absolute temperature, and E\textsubscript{a} is the overall activation energy (Figure 5).

The dissolution rate of polymeric MnO\textsubscript{2} has a preexponential factor of 1.1 at pH 5.4 and 10\textsuperscript{2} M\textsuperscript{-1} s\textsuperscript{-1} for cysteine and glutathione, respectively.

The preexponential factor values lower than normal are showing the influence of steric effects due to the molecule size and the presence of substituents. The different values of A between both thiols would depend on the steric effects. Consequently, this is due to the tripeptide structure of glutathione where the large size of the glutathione molecule may contribute to some steric effects that increase the activation energy while decreasing the preexponential factor and the dissolution rate.

To determine whether the reaction mechanism is associative or dissociative, the entropy of activation is needed (42), which can be evaluated from an Eyring plot [ln(k/T)] versus 1/T based on

$$\ln(k/T) = (\Delta H^\ddagger/RT) + (\ln(k/h) + (\Delta S^\ddagger)/R) \tag{II}$$

where \(\Delta H^\ddagger\) is the enthalpy of activation, \(\Delta S^\ddagger\) is the entropy of activation, \(k\) is the Boltzmann constant (1.381 \times 10\textsuperscript{-23} J K\textsuperscript{-1}), and h is the Planck's constant (6.626 \times 10\textsuperscript{-34} J s). The slope (\(\Delta H^\ddagger/R\)) provides the enthalpy of activation, and the intercept (ln(k/h) + (\(\Delta S^\ddagger/R\))) yields the entropy of activation. A large negative \(\Delta S^\ddagger\) indicates an associative reaction whereas a large positive \(\Delta S^\ddagger\) indicates a dissociative reaction (41). All kinetic activation parameters are given in Table 1, which shows that both thiols have a large negative \(\Delta S^\ddagger\) for MnO\textsubscript{2} reduction and that the reactions are associative and proceed via inner-sphere redox reactions.

The values of activation energy, enthalpy, and entropy of activation for a given reaction are usually indicative of some...
effects such as van der Waals, dipole–dipole, H-bonding, ionic interactions between charged species, and also specific bonding of reactive moieties. The processes that can be explained via van der Waals, dipole–dipole or other weak intermolecular forces are occurring by an outer-sphere mechanisms and are characterized by a very low activation energy, while specific bonding of reactive moieties occur by inner-sphere mechanisms such as the one already mentioned here and require more higher activation energies.

Dissolution can proceed via several parallel pathways that involve labilization of bridging oxygens by ligands that are dynamically stable in the inner-coordination sphere of the detaching manganese. If any of the dissolution reactions were completely transport (diffusion) controlled, there should be no pH dependence of the oxidation rate. Despite this, if Mn(II) released into solution is the rate-determining step, there should be no difference for the dissolution rate between both ligands. Then, the rate is controlled either by the binding of the ligand to the surface or the detachment of the activated surface complex from the surface. Thus, the dissolution rate is not controlled by transport of reduced species away from the surface (Mn(II) release into solution is not the rate-determining step), and the reactions at the surface (which are responsible for the activation energy) must be rate-controlling (42). Therefore, for both ligands, the dissolution would be surface-controlled.

It has been found that comparatively simple rate laws are obtained if the observed rates are plotted against the concentrations of the adsorbed species and surface complexes (43, 44). Then, a possible reaction mechanism, considering Mn(II) and the disulfides as the main products, has been described for the rate-determining step (45). Their results show that as the reaction proceeds Mn(III) is formed on the oxide surface. In the cases where the reduction does not stabilize Mn(III) through complexation [e.g., As(III), Cr(III), Se(VI)], Mn(III) behaves as an intermediate because the profile of Mn(III) concentration versus time has a maximum, i.e., it is formed and consumed in another reaction step (52, 53, 55).

The formation of RS-radicals was proposed by Wallace (28) in his study of thiol oxidation with solid-phase MnO2 in organic solvents because, in the presence of olefins, sulfur addition products (addition to the double bonds) were formed. These results are indicative of RS radical formation. These radicals were also detected by ESR in solutions resulting from the oxidation of CSH and GSH with peroxytrinitrite or OH radicals (57). Because of the relative stability of sulfur radicals (58), RS-radicals were proposed as intermediates in reaction mechanisms to explain the oxidation of mercaptocarboxylic acids with magnetite (24), the oxidation of thioglycolic acid and glutathione with Mn(III) complexes, and the oxidation of thiols with complexes of iron and another metals Ce4+, Co3+, V5+, and Cu2+ (30).

(iii) RS radicals dimerize to form the corresponding disulfide:

\[ 2RS \xrightarrow{k_2} RSSR \]  

Sulfhydryl radicals might dimerize while the sulfur atoms are still attached to the polymeric MnO2. In that case, the distance between both radicals, which would be equivalent to the Mn–Mn distance on an oxide surface, should be similar to the bond length of the corresponding disulfide. The length for a S–S bond in most molecules having two or more sulfur atoms linked to each other is approximately 2 Å (59). However, the distance between vicinal Mn atoms in most manganese(IV) oxides is slightly larger than 4 Å (60); therefore, dimerization of radicals while attached to polymeric MnO2 or a MnO2 surface is very unlikely to occur. Another possible dimerization mechanism (24) that cannot be ruled out as possible is that thiols coordinate to the surface through other complexing groups (e.g., carbonate in cytochrome). This second group could work as an anchor allowing the S–S bond to be formed in solution while the thiol is still attached to a MnO2 surface or polymeric MnO2 through the second coordinating group. This would also permit their further oxidation to sulfonates at low pH by allowing contact with soluble polymeric MnO2. The increase in the Eo for the oxidation of glutathione over that for cytochrome suggests that carbonate ion complexation with MnO2 is most likely.

(iv) Desorption of Mn(II) and generation of a new surface site:

\[ Mn^{II}OH^+ \xrightarrow{k_2} Mn^{III}OH + Mn^{II}aq + H^+ \]
Therefore, the rate of step 2 would be reductive dissolution of hydrous ferric oxide with cysteine. The authors suggested the formation of surface complexes where the metal is complexed either by the thiol through the sulfur, or the nitrogen, or the oxygen of the carboxylate groups.

These surface complexes are the ones involved in the acid–base equilibrium already mentioned. Assuming that the residual charge on the metal center is +1, some structures for complexes of overall charge 0 and –1 can be postulated:

In the pH range studied, the rate constant for reduction of polymeric MnO₂ was observed to decrease with increasing pH (Figure 4). These results can be explained considering that the species, formed in the first reaction step, are involved in the acid–base equilibria characterized by the corresponding K_{app} value:

\[
\text{R} = \frac{k_{1}k_{2}}{k_{-1} + k_{2}'} \times \text{[Mn}^{IV}\text{OH}][\text{RSH}] \quad (9)
\]

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\text{R} = \frac{k_{1}k_{2}}{k_{-1} + k_{2}'} \times \text{[Mn}^{IV}\text{OH}][\text{RSH}] \quad (9)
\]

Assuming that all the intermediates are in steady state, the initial redox reaction becomes first-order with respect to both reactants (the surface species (=Mn^{IV}OH) and the free thiol concentrations [RSH]) (eq 9). Then the stoichiometric rate law has the same shape as the experimental rate law (eq 1):

\[
\mathcal{R} = \frac{k_{1}k_{2}}{k_{-1} + k_{2}'} \times \text{[Mn}^{IV}\text{OH}][\text{RSH}] \quad (10)
\]

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\[
\mathcal{R} = \frac{k_{1}k_{2}}{k_{-1} + k_{2}'} \times \text{[Mn}^{IV}\text{OH}][\text{RSH}] \quad (11)
\]

Both species can undergo the reaction steps already mentioned (eqs 1–8), and their different reactivities cause the reaction rate to change with pH (49). Amribahman et al. (25) successfully used a similar model in their study of the reductive dissolution of hydrous ferric oxide with cysteine. Therefore, the rate of step 2 would be

\[
\mathcal{R} = k_{2}(\text{MnSRH}) \times \text{[Mn}^{IV}\text{SRH}] \quad (12)
\]

A species distribution varying with pH is given by the values of the distribution coefficients (α_{i}) and total concentration (C_{T}), which are a function of K_{app} and pH:

\[
\text{[Mn}^{IV}\text{SRH}] = C_{T} \times \alpha_{\text{MnSRH}}
\]

\[
\text{[Mn}^{IV}\text{SR}^{-}] = C_{T} \times \alpha_{\text{MnSR}^{-}}
\]

\[
C_{T} = \text{[Mn}^{IV}\text{SRH}] + \text{[Mn}^{IV}\text{SR}^{-}]
\]

Therefore, the rate for step 2 can be written as a linear combination of both distribution factors:

\[
\mathcal{R} = C_{T}[k_{2}(\text{MnSRH})\times \alpha_{\text{MnSRH}} + k_{2}(\text{MnSR}) \times \alpha_{\text{MnSR}}] \quad (13)
\]

The above equation accounts for the pH dependence of the overall rate constant k. Figure 4 shows the variation in k for cysteine and glutathione with pH. The symbols are experimental points, and the lines were plotted as the best fit assuming that C_{T} is equal to the total available MnO₂ surface sites and using three adjustable parameters in eq 14. These parameters were K_{app}, K_{2}(MnSRH), and K_{2}(MnSR) accounting for the differences in reactivity of both surface complexes. Table 2 shows the results for these three parameters for both thiols. As shown in Figure 4, the proposed model is a good fit to the experimental data. The fit was done using the non-linear curve fit tool included in Origin 5.0 software (OriginLab software). Levenberg–Marquardt routine was used to minimize the value of χ², which was taken as a convergence criterion. Different initial scenarios with different values for the fitting parameters were used to verify the uniqueness of convergence.

The protonation–deprotonation process for the reaction with cysteine would take place on the nitrogen atom of the amino group as previously proposed by Amirbahman et al. (25) in their study of the reductive dissolution of hydrous ferric oxide with cysteine. The authors suggested the formation of surface complexes where the metal is complexed either by the thiol through the sulfur, or the nitrogen, or the oxygen of the carboxylate groups.

These surface complexes are the ones involved in the acid–base equilibrium already mentioned. Assuming that the residual charge on the metal center is +1, some structures for complexes of overall charge 0 and –1 can be postulated:

In the neutral complex, the amino group is protonated; in the negatively charged complex, it is deprotonated. There are two possible structures for the latter complex if S binds to the Mn, one with the nitrogen coordinated to the Mn center and the other one with the oxygen coordinated to the metal center.

Table 2 and Figure 4 demonstrate that the protonated species are the most reactive species for both thiols. Similar results were obtained for the reaction between solid MnO₂ and sulfide (21). Also, the pK_{app} values corresponding to the protons on the amino groups, are dramatically shifted to more acidic values. Coordination of cysteine with Fe(III) on an hydrous ferric oxide surface causes the amino group proton to be 3 orders of magnitude more acidic than usual, given that Fe(III) acts as a Lewis acid (25).

In our study, the shift in pK_{app} is even higher, which can be attributed to the fact that Mn(IV) is more acidic than Fe(III). In the reaction with glutathione, the group involved in that acid–base equilibria would be the amino group corresponding to the glutamic acid. In both cases, the pK_{app} values followed the same behavior than the free thiols pK_{a}. The surface complexes involved in the acid–base equilibria are more labil when increase the strength of the free thiol. The tendency to form chemical linkages to solid surface atoms correlates with likelihood of forming comparable complexes in solution (61). Likewise, the exchange of protons by a dissociative or associative processes would follow a similar tendency.

Unlike the reaction with H₂S, the speciation of the oxidation products does not change significantly in the pH range typical of natural waters as the corresponding disulfides are the only products detected in this pH range. Sulfonic acids are formed at much more acidic conditions (pH < 2) such as found in salt marshes and other oxidizing sediments (2); therefore, the reduction of MnO₂ by thiols may not be a significant source of sulfonates in some natural systems. Given their widespread occurrence (32, 62), other mechanisms must also be operational for sulfonate formation such as sulfite and/or thiosulfate addition to α,β-unsaturated organic compounds (31, 32). For soluble polymeric MnO₂, the rate constants at pH 10 follow the order k_{sulfide} = 10^x M⁻¹
This rate constants are proportional to the thiol dissociation constants (RSH pK values of 7.0, 8.18, and 8.66 with R = H, CS, and GS respectively), the pK_{thiol} versus pK_{plot} has a slope of 0.94 and R^2 = 0.89. Then the reactivity decreases in the order HS^− > CSH > GSH, reflecting the electronic and steric effects of the thiol substituents on the reaction considered.

Although the oxidation of inorganic sulfide with manganese oxides has been studied extensively (16, 21, 46, 63), oxidation of thiol of environmental importance has not received much attention. This lack of information hampers our knowledge of the reaction pathways for several species in the sulfur biogeochemical cycle (31). Polymeric MnO_2 may not represent the most typical MnO_2 phases present in natural systems, but the results obtained with this polymeric phase are relevant and would contribute to understanding the chemical behavior of the anoxic basins.

Further work is needed with other solid manganese oxide phases typical of natural systems to further assess the contribution of the studied process to the biogeochemical cycles of Mn and S. As expected, several results have similarity to those obtained in a previous study on the reaction with H_2S (21). Redox rate constants increase as pH decreases, and this fact can be explained by considering a model where reaction constants (RSH pK values) are plotted. The use of soluble thiol compounds (aS^−, aCS^−) to establish whether the reaction is dissociative or associative, as was done with the reaction of MnO_2 and nitrite (82), may be needed to confirm this hypothesis. Another associative and inner-sphere redox reaction.

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1 s^−1 (21), k_{cysteine} = 200 M^−1 s^−1, and k_{glutathione} = 20 M^−1 s^−1 (k_{cysteine} and k_{glutathione} were obtained by extrapolation of the plots in Figure 4).

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