

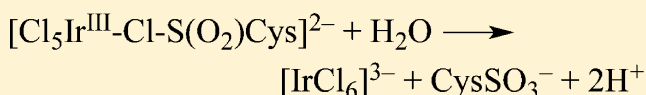
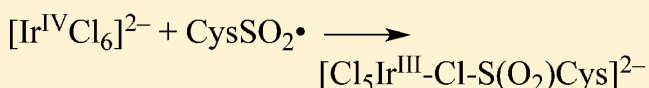
Oxidation of Cysteinesulfinic Acid by Hexachloroiridate(IV)

Nootan Bhattarai and David M. Stanbury*

Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama 36849, United States

S Supporting Information

ABSTRACT: We report the results of an experimental study of the oxidation of cysteinesulfinic acid (CysSO₂H) by [IrCl₆]^{2−} in aqueous media at 25 °C in order to gain insight into the mechanisms of oxidation of alkylsulfinic acids by simple one-electron oxidants. When the reaction is performed with exclusion of O₂ between pH 3 and 5, it is complete in several seconds. The products are [IrCl₆]^{3−} and CysSO₃H. Kinetic data obtained by stopped-flow UV–vis methods with [CysSO₂H] ≫ [Ir^{IV}]₀ reveal the rate law to be $-d[\text{Ir}^{\text{IV}}]/dt = k[\text{Ir}^{\text{IV}}]^2[\text{CysSO}_2\text{H}]/[\text{Ir}^{\text{III}}]$ with a negligible pH dependence. The value of k is $(6.8 \pm 0.12) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at $\mu = 0.1 \text{ M}$ (NaClO₄). A mechanism is inferred in which the first step is a rapid and reversible electron-transfer equilibrium between Ir^{IV} and CysSO₂[−] to form Ir^{III} and CysSO₂•. The second step is the rate-limiting inner-sphere oxidation of CysSO₂• by Ir^{IV}. Production of CysSO₃H is proposed to occur through hydrolysis of an Ir^{III}-bound sulfonyl chloride that is the immediate product of the inner-sphere second step.



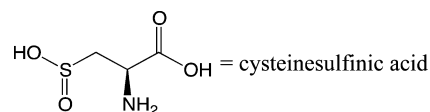
■ INTRODUCTION

It is well known that alkylsulfinic acids (RSO₂H) are susceptible to oxidation in aqueous solution, and the products are often sulfonic acids (RSO₃H).¹ Indeed, this process is one of the steps in the essential conversion of cysteine to taurine.² An open question is how the formation of RSO₃H from RSO₂H might occur when the oxidants are restricted to one-electron pathways. Prior reports on reactions of alkylsulfinic acids with one-electron oxidants are quite limited; to our knowledge, they consist of studies on the oxidations of hydroxymethanesulfinic acid,³ hypotaurine,⁴ and cysteinesulfinic acid (CysSO₂H) by ClO₂,⁵ and the oxidations of methanesulfinic acid by Cl₂•[−], N₃•,⁷ and OH•.⁷ In two of these studies, the identity of the ultimate oxidation product was determined: ClO₂ oxidation of CysSO₂H yields CysSO₃H⁵ and steady-state radiolytic oxidation of CH₃SO₂H by OH• yields CH₃SO₃H.⁷ Also, it is relatively common to find sulfonic acids among the products of oxidation of thiols by one-electron oxidants. For example, we have reported that RSO₃H is produced in the oxidations of thioglycolic acid and glutathione by [IrCl₆]^{2−}.^{8,9} It would seem reasonable to propose that the RSO₃H products in these reactions arise through oxidation of RSO₂H intermediates, but evidence for this mechanism is lacking.

There is ESR evidence that alkylsulfinic acids can react with one-electron oxidants (RO• and Cl₂•[−]) to form sulfonyl radicals (RSO₂•) as intermediates.^{10,11} UV–vis spectroscopy has also shown that RSO₂• radicals are formed in the oxidations of RSO₂H by OH• and N₃•.⁷ Sulfonyl radicals are believed to undergo a variety of reactions, including reduction,⁷ dimerization, SO₂ elimination, olefin addition, O₂ addition, and disproportionation.¹² The latter is thought to occur for arylsulfonyl radicals through net oxygen-atom transfer to generate ArSO₃•,^{12,13} which would be a powerful one-electron oxidant and, thus, provide a

route to ArSO₃H. However, there appears to be no evidence for disproportionation of RSO₂• radicals, and arguments can be made that disproportionation should be thermodynamically unfavorable. There is some evidence that RSO₂• radicals can be oxidized to RSO₃H by addition of OH•,⁷ but this process is of quite limited generality. One might propose that RSO₂• radicals could be oxidized to their corresponding cations (RSO₂⁺), but such species have never been detected in solution. Apparently, a viable mechanistic proposal for conversion of RSO₂• to RSO₃H by species other than OH• remains elusive.

In summary, it is clear that some one-electron oxidations of alkylsulfinic acids yield sulfonic acids, and that the initial step is likely to be the one-electron oxidation to form RSO₂•. What is unclear is the generality of these ideas and the mechanism of formation of final products. The present report describes our initial studies of these issues, probed through the reaction of [IrCl₆]^{2−} with cysteinesulfinic acid:



We find that the sulfonic acid is indeed produced, although the rate law for the reaction is rather unusual.

■ EXPERIMENTAL SECTION

Reagents and Solutions. NH₄Cl (Fisher), acetic acid (Fisher), (NH₄)₃IrCl₆·H₂O (Ir^{III}, Aldrich), D₂O (Sigma), CuSO₄·5H₂O (Fisher), (NH₄)₂Fe(SO₄)₂·6H₂O (Fisher), HCl_(aq) (Fisher), NaOH pellets (“SigmaUltra”, Sigma-Aldrich),

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N-tert-butyl- α -phenylnitrone (PBN, Aldrich), 2,6-pyridine dicarboxylic acid (Aldrich), cysteic acid (CysSO₃H, Aldrich), L-cysteinesulfonic acid monohydrate (CysSO₂H, Aldrich), 3-(trimethylsilyl)-1-propane sulfonic acid sodium salt (DSS, Aldrich), Cl₂ gas (Matheson), Dowex 50-X8 resin (J.T. Baker), 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO, TCI), and Na₂C₂O₄ (Fisher) were used without further purification. (NH₄)₂IrCl₆ (Ir^{IV}, Aldrich) and NaClO₄ (Fisher) were used after recrystallization.

Stock solutions of NaClO₄ were standardized as described previously.⁸ Likewise, (NH₄)₂IrCl₆ was recrystallized as described previously.⁸ Deionized water was purified with a Barnstead Nanopure Infinity Ultrapure water system and used to prepare all solutions. Freshly prepared solutions were used in all experiments except NaClO₄, HClO₄, HCl and buffers. All reactant solutions were purged with argon gas prior to use.

Methods. A HP-8453 diode array spectrophotometer equipped with a Brinkman Lauda RM6 thermostatted system was used to record all UV–vis spectra at 25 ± 0.1 °C. All pH measurements were performed on a Corning 450 pH/ion meter with a Mettler Toledo Inlab 421 pH electrode (filled with 3 M NaCl solution) using the relationship pH = −log[H⁺]. ¹H NMR spectra were obtained on a Bruker AV 400 MHz spectrometer. Chemical shifts in D₂O are expressed relative to DSS.

Kinetic studies were performed at 25 ± 0.1 °C on a Hi-Tech SF-51 stopped-flow spectrophotometer in its 1 cm path length configuration with OLIS 4300 data acquisition and analysis software. All kinetic data were monitored at 488 nm. The concentration of CysSO₂H was kept in at least a 10-fold excess over the oxidant [Ir^{IV}]₀. Kinetic traces were fit with the integrated pseudo-second-order rate law

$$A_t = \Delta A / (\Delta A k_{\text{prog}} t + 1) + A_{\text{inf}} \quad (1)$$

In eq 1, ΔA is a fitted parameter and represents the difference between the initial and final absorbance. The values of k_{prog} were converted to pseudo-second-order rate constants (k_{obs2}) through the relationship $k_{\text{obs2}} = k_{\text{prog}}(\epsilon_{\text{eff}} l)$ where ϵ_{eff} is the molar absorptivity of [IrCl₆]^{2−} ($3.98 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 488 nm)⁸ and l is the optical path length. All k_{obs2} values reported are the average of at least four runs.

RESULTS

The reaction of CysSO₂H with [IrCl₆]^{2−} has been investigated in aqueous solution at 25 °C under anaerobic conditions with CysSO₂H in large excess over Ir^{IV}. Under these conditions the reaction is easily detected by the loss of color arising from the Ir^{IV}. When examined by repetitive-scan UV–vis spectrophotometry (Figure 1), the reaction of 50 μM Ir^{IV} with 0.5 mM CysSO₂H at pH 4.5 (10 mM acetate buffer with 0.5 mM Ir^{III}) shows the decay of the typical Ir^{IV} spectrum between 390 and 540 nm, with an initial half-life of about 3 min, and the final spectrum indicates essentially complete consumption of the Ir^{IV}. As shown in the inset to Figure 1, the semilog plot of [IrCl₆]^{2−} vs t is nonlinear. A full account of the reaction kinetics is given below.

Stoichiometry. ¹H NMR spectroscopy was used to examine the reaction products. A sample was prepared as follows: 3.0 mM and 1.4 mM solutions of Ir^{IV} and CysSO₂H, respectively, were prepared in D₂O. Both of these were purged with Ar gas. One milliliter of each solution was mixed together, and 0.07 mM DSS was added as an internal standard. The sample was unbuffered (pH 2.7). Figure 2 displays the spectrum of the product mixture, which consists of multiplets at 4.23, 3.57, and 3.33 ppm. This spectrum was conclusively identified as arising from CysSO₃H by

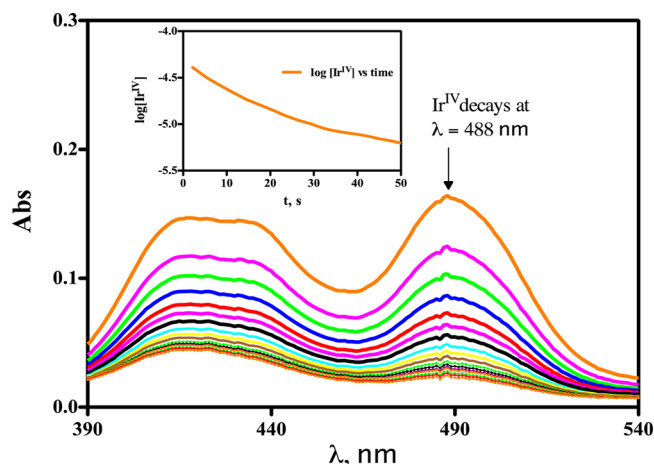


Figure 1. The absorbance decay of Ir^{IV} with excess CysSO₂H. [Ir^{IV}]₀ = 0.05 mM with 0.5 mM [Ir^{III}], [CysSO₂H]₀ = 0.5 mM, acetate buffer (10 mM) at pH 4.5 and μ = 0.1 M (NaClO₄). Inset: semilog plot showing nonpseudo first-order kinetics. Run time = 50 s with cycle time = 3 s.

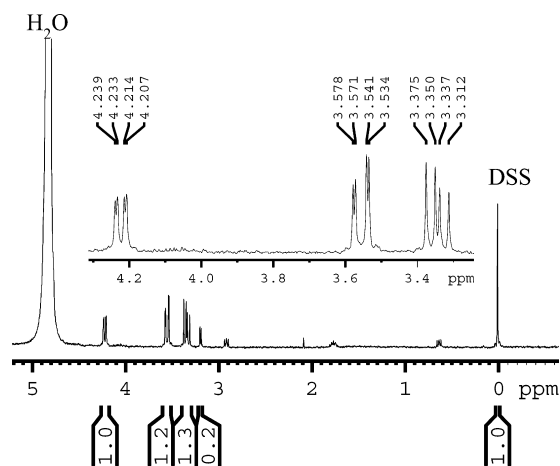


Figure 2. ¹H NMR spectrum of product in the reaction of CysSO₂H and Ir^{IV} at pH 2.7. Inset: highlighted peaks of the product.

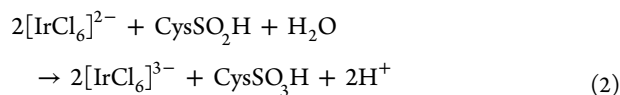
spiking the sample with authentic cysteic acid. Complete consumption of CysSO₂H is indicated by the lack of peaks attributable to this species. By comparison of the integrals of the peaks at 0 ppm (DSS) and those arising from CysSO₃H, the yield of CysSO₃H is 99 ± 10%. These results imply complete conversion of CysSO₂H to CysSO₃H under the conditions of a small excess of Ir^{IV}.

The consumption ratio ($\Delta\text{Ir}^{\text{IV}}/\Delta\text{CysSO}_2\text{H}$) was determined by spectrophotometric titration of 0.508 mM CysSO₂H with small aliquots of 2.04 mM Ir^{IV} at pH 4.7 (acetate buffer). The titration was monitored at the absorbance maximum of Ir^{IV} (488 nm), and the end point was signaled by a sharp rise in absorbance when all the CysSO₂H was consumed. The result was $\Delta\text{Ir}^{\text{IV}}/\Delta\text{CysSO}_2\text{H} = 1.9 \pm 0.1$.

UV–vis spectroscopy was used to determine the Ir-containing product. A reaction mixture was prepared from 0.11 mM Ir^{IV} and 1.15 mM CysSO₂H at pH 4.6 (acetate buffer) and μ = 0.1 M (NaClO₄). The product mixture had an absorbance of 7.0×10^{-3} , consistent with an anticipated product of 0.11 mM [IrCl₆]^{3−}. More conclusively, after bubbling the product solution with Cl₂ and then sparging with N₂, the original [IrCl₆]^{2−} spectrum was recovered in 100 ± 1% yield. This chlorination

method is specific for $[\text{IrCl}_6]^{3-}$, because aquated products would yield significantly different spectra.^{14,15}

The above NMR, titration, and chlorination results give strong support for an overall reaction stoichiometry of



Kinetics. As mentioned above, distinctly non-pseudo-first-order kinetics occurs when Ir^{IV} is mixed with a large excess of CysSO_2H . Further experiments show that the rates are strongly inhibited by the product, $[\text{IrCl}_6]^{3-}$. This behavior is illustrated in Figure 3, which shows stopped-flow measurements of the

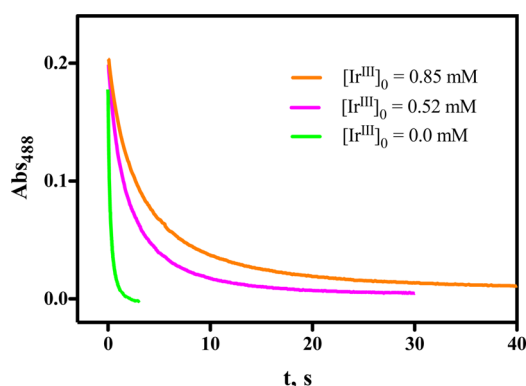


Figure 3. Reaction inhibition by $[\text{IrCl}_6]^{3-}$. $[\text{CysSO}_2\text{H}]_0 = 1.0 \text{ mM}$, $[\text{Ir}^{\text{IV}}]_0 = 0.05 \text{ mM}$, $[\text{Ir}^{\text{III}}]_0 = 0.0\text{--}0.85 \text{ mM}$, $\mu = 0.1 \text{ M}$ (NaClO_4), pH 4.5 (acetate buffer).

absorbance at 488 nm as a function of time for three reactions with initial concentrations of Ir^{III} of 0.0, 0.52, and 0.85 mM, the other conditions being $[\text{Ir}^{\text{IV}}]_0 = 0.05 \text{ mM}$, $[\text{CysSO}_2\text{H}] = 1.0 \text{ mM}$, pH 4.5 (acetate buffer), and $\mu = 0.1 \text{ M}$ (NaClO_4). Because

of this strong product inhibition, all further kinetics studies were conducted with a large excess of Ir^{III} to maintain flooding conditions.

When stopped-flow measurements are performed with excess Ir^{III} , the absorbance changes obey pseudo-second-order kinetics. Figure 4 presents a typical example, contrasting the poor first-order fit and the fine second-order fit for an experiment with $50 \mu\text{M Ir}^{\text{IV}}$, $0.52 \text{ mM Ir}^{\text{III}}$, $1.0 \text{ mM CysSO}_2\text{H}$ at pH 3.2 (acetate buffer), and $\mu = 0.1 \text{ M}$ (NaClO_4). That is, the rates obey the rate law

$$-d[\text{Ir}^{\text{IV}}]/dt = k_{\text{obs}2}[\text{Ir}^{\text{IV}}]^2 \quad (3)$$

The full rate law was determined under the standard conditions of $[\text{Ir}^{\text{IV}}]_0 = 0.05 \text{ mM}$ and $\mu = 0.1 \text{ M}$ (NaClO_4) with acetate buffers. The dependence of $k_{\text{obs}2}$ on the CysSO_2H concentration is displayed in Figure 5 (data is in Supporting Information

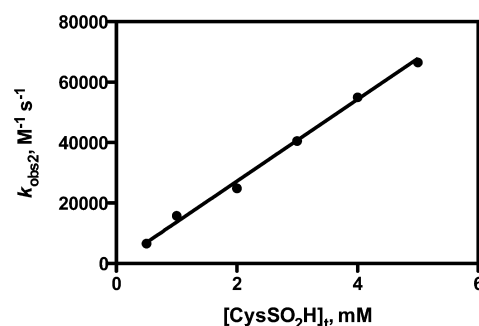


Figure 5. Dependence of $k_{\text{obs}2}$ on $[\text{CysSO}_2\text{H}]$ in the presence of excess Ir^{III} . $[\text{CysSO}_2\text{H}] = 0.50\text{--}5.0 \text{ mM}$, $[\text{Ir}^{\text{IV}}]_0 = 0.05 \text{ mM}$, $[\text{Ir}^{\text{III}}]_0 = 0.50 \text{ mM}$, $\mu = 0.1 \text{ M}$ (NaClO_4), acetate buffer, pH 4.6.

Table S-1), which shows the results of a series of experiments at pH 4.6 with $[\text{Ir}^{\text{III}}] = 0.50 \text{ mM}$. A first-order dependence of $k_{\text{obs}2}$ on $[\text{CysSO}_2\text{H}]$ is evident from the excellent linear fit and

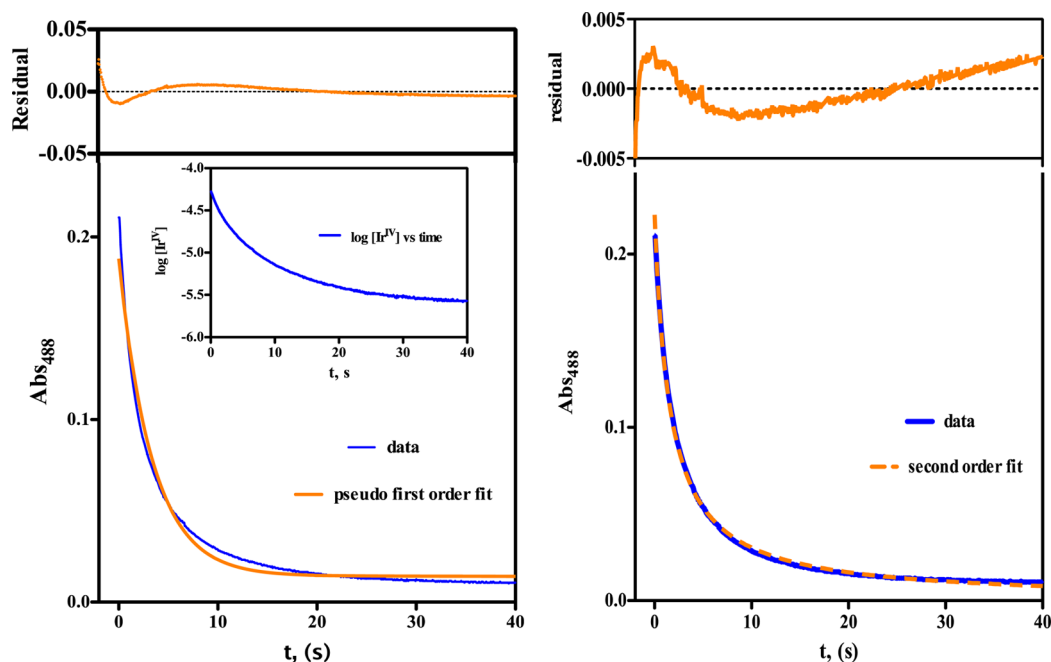


Figure 4. Kinetics with excess Ir^{III} . Lower boxes: blue line = experimental trace, orange line = fit. Left: pseudo-first-order fit. Inset: $\log [\text{Ir}^{\text{IV}}]$ vs t plot. Right: second-order fit of the same data. Upper boxes, residuals. Conditions: $[\text{Ir}^{\text{IV}}]_0 = 0.05 \text{ mM}$, $[\text{Ir}^{\text{III}}] = 0.52 \text{ mM}$, $[\text{CysSO}_2\text{H}]_0 = 1.0 \text{ mM}$, pH 3.2 (acetate buffer), and $\mu = 0.1 \text{ M}$ (NaClO_4).

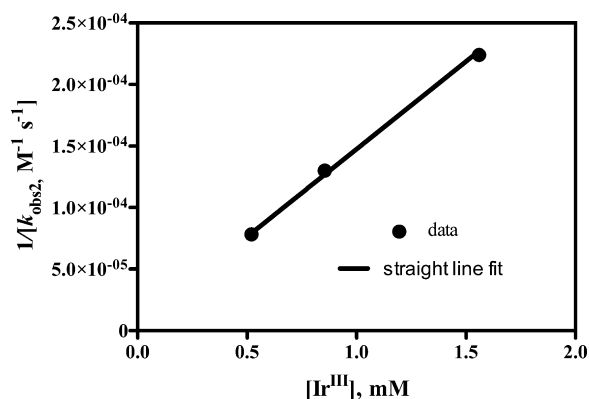


Figure 6. Inverse dependence $k_{\text{obs}2}$ on $[\text{IrCl}_6^{3-}]$. $[\text{CysSO}_2\text{H}] = 1 \text{ mM}$, $[\text{Ir}^{\text{IV}}]_0 = 0.05 \text{ mM}$, $[\text{Ir}^{\text{III}}] = 0.52\text{--}1.56 \text{ mM}$, $\mu = 0.1 \text{ M}$ (NaClO_4), acetate buffer, pH 4.5.

negligible intercept. The dependence of $k_{\text{obs}2}$ on the Ir^{III} concentration was studied with 1.0 mM CysSO_2H at pH 4.5 and is shown as a plot of $1/k_{\text{obs}2}$ vs $[\text{Ir}^{\text{III}}]$ in Figure 6 (Table S-2 of Supporting Information). Here again, the plot is linear and has a negligible intercept, in this case indicating an inverse dependence of $k_{\text{obs}2}$ on $[\text{Ir}^{\text{III}}]$. As shown by the data in Supporting Information Table S-3, the rates are independent of pH between pH 3.1 and 5.6. These results are summarized by eq 4

$$k_{\text{obs}2} = k[\text{CysSO}_2\text{H}]/[\text{Ir}^{\text{III}}] \quad (4)$$

and the overall rate law is

$$-d[\text{IrCl}_6^{2-}]/dt = k[\text{IrCl}_6^{2-}]^2[\text{CysSO}_2\text{H}]/[\text{IrCl}_6^{3-}] \quad (5)$$

When the values of $k_{\text{obs}2}$ in Figures 5 and 6 are used to derive values of k as in eq 4, the average result is $k = (6.8 \pm 0.12) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

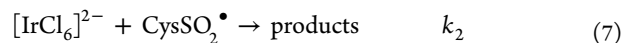
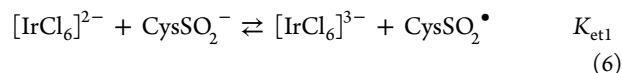
Several tests for metal-ion catalysis all yielded negative results. Thus, addition of $5 \mu\text{M}$ CuSO_4 or $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ into the reaction of 1 mM CysSO_2H with 0.1 mM Ir^{IV} (and no Ir^{III}) at pH 4.3 had essentially no accelerating effect on the rates. Likewise, the addition of 1 mM $\text{Na}_2\text{C}_2\text{O}_4$ or dipic as metal ion chelators had no inhibiting effect on the rates.

Experiments were also performed to test the effects of the potential radical scavengers PBN and DMPO. In the case of PBN, experiments were performed with $[\text{Ir}^{\text{IV}}]_0 = 0.1 \text{ mM}$ and $[\text{CysSO}_2\text{H}] = 1.0 \text{ mM}$ at pH 4.3 (acetate buffer), $\mu = 0.1 \text{ M}$ (NaClO_4), and $[\text{dipic}] = 1 \text{ mM}$. The half-lives differed by less than 5% for PBN concentrations of 0, 1, 2, and 5 mM. For the DMPO experiments, the conditions were the same except that dipic was absent, $[\text{Ir}^{\text{IV}}]_0$ was 0.05 mM , and $[\text{Ir}^{\text{III}}]$ was 0.5 mM . The rate constants were identical within $\pm 5\%$ for reactions with 0, 1, and 2 mM DMPO. Thus, millimolar concentrations of PBN or DMPO have no discernible effects on the reaction kinetics.

DISCUSSION

CysSO_2H has three pK_a s: 1.50, 2.38, and 9.24.¹⁶ At low pH, it is protonated at the carboxylate, amine, and sulfinate sites and has an overall charge of +1. The first two pK_a s correspond to deprotonation at the sulfinate and carboxylate sites, so within the pH range of this study, the compound is primarily in its monoanionic form, designated CysSO_2^- .

The rate law for oxidation of CysSO_2H by $[\text{IrCl}_6]^{2-}$ is unusual, and it can be explained by the following schematic mechanism:



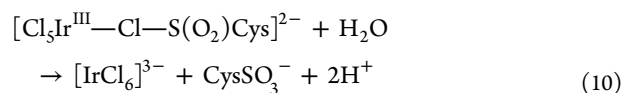
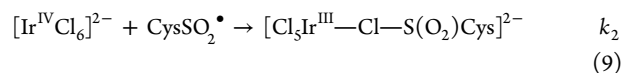
This mechanism leads to the rate law

$$-d[\text{IrCl}_6^{2-}]/dt = 2K_{\text{et}1}k_2[\text{IrCl}_6^{2-}]^2[\text{CysSO}_2^-]/[\text{IrCl}_6^{3-}] \quad (8)$$

Under the experimental conditions $[\text{CysSO}_2^-] = [\text{CysSO}_2\text{H}]$, and so eq 8 is equivalent to the observed rate law (eq 5) with the empirical rate constant k identified as $2K_{\text{et}1}k_2$.

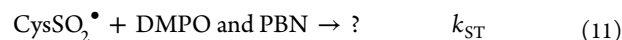
The above mechanism postulates that the first step is a reversible electron-transfer equilibrium that produces CysSO_2^\bullet , the cysteinesulfonyl radical. The chemistry of sulfonyl radicals is relatively well understood,^{11,12,17} and CysSO_2^\bullet itself has been detected by ESR.¹¹ In order for the second step to be rate limiting, the first step must be uphill, which implies that $K_{\text{et}1}$ is less than unity; that is, the cysteinesulfonyl radical must be a stronger oxidant than $[\text{IrCl}_6]^{2-}$ (for which E° is 0.89 V).¹⁸ Although there are no prior estimates of E° for CysSO_2^\bullet , this inference is consistent with a prior report that $\text{CH}_3\text{SO}_2^\bullet$ is capable of oxidizing $[\text{Fe}(\text{CN})_6]^{4-}$.⁷ Another requirement of the above mechanism is that the $K_{\text{et}1}$ equilibrium be established rapidly. Because the reaction is just an electron-transfer reaction, quite possibly an outer-sphere type, it seems quite plausible that the reaction would be rapid.

The second step in the above mechanism, reaction 7, is anticipated to be a one-electron redox reaction, but it is unlikely to be a simple outer-sphere reaction because the implied product, CysSO_2^+ , would seem to be energetically inaccessible. Accordingly, we propose a two-step quasi-inner-sphere mechanism for reaction 7



Reaction 9 leads to the formation of an iridium-bound sulfonyl chloride and is classified as an inner-sphere electron-transfer reaction with chloride serving as the bridging ligand. Reaction 10 is hydrolysis of the bound sulfonyl chloride to form the final products; its rate is unknown because none of the species in this step should have significant absorbance in the visible. Although free sulfonyl chlorides hydrolyze rather slowly,¹⁹ it is conceivable that the $\text{Cl}_5\text{Ir}^{\text{III}}$ substituent would enhance the solvolysis rate.

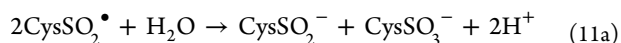
An interesting feature of the results in terms of the proposed mechanism is the lack of any effect of the spin traps PBN and DMPO on the kinetics. One would expect the rates to increase if these species were effective in scavenging the CysSO_2^\bullet radicals



For this effect to be significant, the scavenging rates (k_{ST}) would have to be comparable to or greater than the rate of reaction with $[\text{IrCl}_6]^{2-}$ (k_2 , eq 9). Given the relative concentrations of $[\text{IrCl}_6]^{2-}$ and spin traps and the possibility that k_2 could be as large as $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, the lack of scavenging implies that k_{ST} is less than $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This outcome appears reasonable

because it is likely that the value of k_{ST} is similar to the rate constant for reaction of $\text{SO}_3^{\bullet-}$ with DMPO, which is only $1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.²⁰

As an alternative to the above mechanism, one might suggest that the CysSO_2^{\bullet} radical proceeds to final products through a second-order disproportionation



This suggestion can be ruled out easily because it would lead to a rate law that has an inverse second-order dependence on $[\text{Ir}^{\text{III}}]$, contrary to the observed rate law.

Another line of inquiry is the relationship between this study and a prior study on the oxidation of cysteine by $[\text{IrCl}_6]^{2-}$.²¹ Cysteinesulfonic acid (CysSO_3H) was identified as the product in that reaction, and it is possible that it arises through oxidation of CysSO_2H . Unfortunately, a quantitative test of this hypothesis is inappropriate because the cysteine oxidation was studied at much lower pH than the current experiments. Also, the experiments in that study were performed without taking measures to prevent the copper catalysis that normally occurs in such thiol oxidations.^{8,9} Qualitatively, our results suggest that if CysSO_2H is produced in the oxidation of cysteine by $[\text{IrCl}_6]^{2-}$, a substantial fraction of it should be oxidized further to CysSO_3H .

The oxidation of CysSO_2H to CysSO_3H by ClO_2 has been investigated by Darkwa et al.⁵ These workers used the initial-rate method to establish that the rates have a first-order dependence on $[\text{CysSO}_2\text{H}]$, in good analogy with the Ir^{IV} reaction. Pursuing this analogy, one might anticipate that the rates would also show a second-order dependence on $[\text{ClO}_2]$ and an inverse dependence on $[\text{ClO}_2^-]$. However, a complicating factor is that ClO_2^- also reacts with CysSO_2H , whereas Ir^{III} does not. It is conceivable that the modeling results reported for the ClO_2 reaction could be improved by elaborating the mechanism along the lines described here, including a reversible initial electron-transfer step.

We have noted previously that the degree of overoxidation of thiols (formation of sulfinic and sulfonic acids rather than disulfides) by typical outer-sphere oxidants seems to be related to E° for the oxidant.⁸ The present study suggests that another factor might be the availability of ligands that can mediate the oxidation of the sulfonyl radicals as in eq 9. Oxidants lacking such ligands might yield disulfones ($(\text{RSO}_2)_2$) instead of sulfonic acids.

■ ASSOCIATED CONTENT

Supporting Information

Tables investigating the effects of several variables on the kinetics. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*David M. Stanbury. E-mail: stanbdm@auburn.edu.

Notes

The authors declare no competing financial interest.

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