Inorg. Chem. **2002**, *41*, 5538–5543

Inorganic Chemistry
Article

Reduction of Octacyanomolybdate(V) by Thioglycolic Acid in Aqueous Media

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Received May 8, 2002

In aqueous media at 25 °C $[Mo(CN)_8]^{3-}$ is reduced by thioglycolic acid ($HSCH_2COOH$, TGA), and the reaction is strongly accelerated by the presence of trace amounts of copper ions. Dipicolinic acid (dipic) is an effective inhibitor of the copper catalysis. Both with and without dipic the reaction has the stoichiometry $2[Mo(CN)_8]^{3-} + 2TGA \rightarrow 2[Mo(CN)_8]^{4-} + RSSR$, where RSSR is the disulfide derived from formal oxidative dimerization of TGA. In the presence of dipic, PBN (*N*-*tert*-butyl-α-phenyl-nitrone), and with a large excess of TGA the rate law for consumption of $[Mo(CN)_8]^{3-}$ is first order in both [TGA] and $[Mo(CN)_8{}^{3-}]$. The complex pH dependence is consistent with $^-SCH_2CO_2{}^-$ being highly reactive ($k = 1.8 \times 10^4$ M^{-1} s^{-1}), the monoanion being less reactive, and $HSCH_2CO_2H$ being unreactive. A mechanism is proposed in which the dianion undergoes electron transfer to $[Mo(CN)_8]^{3-}$, thus generating the thiyl radical. Analysis of the electron-transfer rate constant in terms of Marcus theory yields an effective self-exchange rate constant for the thiolate/thiyl redox couple that is in reasonable agreement with the value derived previously from the reaction of TGA with $[IrCl_6]^{2-}$. When copper catalysis is inhibited, the two reactions differ substantially in that the yield of $^-O_3SCH_2CO_2{}^-$ is significant for $[IrCl_6]^{2-}$ but undetectable for $[Mo(CN)_8]^{3-}$.

Introduction

The aqueous oxidation of thiols is of obvious importance, and there are many reports on the kinetics and mechanisms of these reactions. However, when classical "outer-sphere" metal-complex one-electron oxidants are used, the reactions are almost invariably catalyzed by trace levels of copper ions. We recently reported an exception to this rule, in which the intrinsic (uncatalyzed) oxidation of thioglycolate (TGA) by $[IrCl_6]^{2-}$ was studied by use of a masking agent effective for Cu^{2+}.[1] Two notable results to emerge from that study were (1) that the Cu-catalyzed reaction yields only the corresponding disulfide while the intrinsic reaction yields a mixture of the disulfide and the sulfonate and (2) that the thiolate form of TGA is the reactive electron donor. One question posed by these results is whether one should expect to obtain such product mixtures in general with outer-sphere oxidants. Another question is whether Marcus theory is useful in predicting the rates of these reactions.

As a first step in addressing these questions the present paper reports on the oxidation of TGA by $[Mo(CN)_8]^{3-}$. The reactions of the octacyanomolybdate(V) anion with inorganic substrates have been well documented,[2-7] and its use as an outer-sphere oxidant is well established. Olatunji et al. have reported on the reduction of this complex by a series of three aliphatic thiols: L-cysteine, penicillamine, and thioglycolic acid.[8] Surprisingly, the rate laws obtained for these reactions included no terms dependent on Cu^{2+}, no mention was made of the possibility of Cu^{2+} catalysis, and no potential masking agents were present in the reaction solutions. In the present paper we report that the reaction of TGA with $[Mo(CN)_8]^{3-}$ is highly senstitive to Cu^{2+} catalysis, and we develop the use of 2,6-pyridinedicarboxylic acid (dipic) as a Cu^{2+}-masking reagent that is effective over a wide range of pH. Our results demonstrate that the prior report on the reaction of TGA with $[Mo(CN)_8]^{3-}$ is actually on the reaction as

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10.1021/ic025702z CCC: $22.00

catalyzed by trace amounts of Cu^{2+}, and they provide initial answers to the two questions posed above.

Experimental Section

Reagents and Solutions. Mercaptoacetic acid, sodium salt (Aldrich) (=TGA, sodium thioglycolate), *N-tert*-butyl-α-phenylnitrone (Aldrich) (=PBN), 2,6-pyridinedicarboxylic acid (Aldrich) (=dipic), 1,10-phenanthroline (Aldrich), 5-chloro-1,10-phenanthroline (Aldrich), and 4-methyl-1,10-phenanthroline (Aldrich) were used without further purification. CsCl and tri-*n*-butylamine were purchased from Aldrich and Acros, respectively. Deuterium oxide, D_2O, was obtained from Aldrich. 3-(Trimethylsilyl)-1-propanesulfonic acid, sodium salt (DSS) was supplied by Aldrich and used as the standard in NMR experiments. Solutions of $HClO_4$ (Fisher, reagent) were standardized by titration with standardized NaOH solution. $NaClO_4$ (Fisher) was recrystallized from warm water and standardized by passage of aliquots through a cation exchange column in H^+ form followed by titration with standardized NaOH. Sodium acetate was recrystallized from water. Sodium borate, $Na_2B_4O_7\cdot10H_2O$ (Fisher), disodium hydrogen phosphate, Na_2HPO_4 (MCB, reagent), Na_2CO_3 (Fisher), and $NaHCO_3$ (Baker Chemical Co., reagent) were used as supplied.

Distilled deionized water was obtained by passage of deionized water through a Millipore ultrapure water purification system, and all the solutions were prepared in this water. Aqueous solutions of $Cs_3[Mo(CN)_8]$ were prepared just prior to use and kept in the dark to prevent any photochemical change. For reactions monitored with a diode-array spectrophotometer, 10 mL of TGA solution was prepared with the appropriate concentrations of PBN, dipic, buffer, and ionic strength and purged with argon gas. Three milliliters of this solution was transferred to a 1 cm path length quartz cell equipped with a Teflon stopcock, and the reaction was initiated by the addition of a small volume of concentrated Mo(V) solution to the cell. For reactions conducted in the stopped-flow spectrophotometer, both Mo(V) and TGA solutions were prepared maintaining the appropriate concentrations of the other reagents, sparged with argon gas, and transferred via gastight glass syringes.

Preparation of $Cs_3Mo(CN)_8\cdot2H_2O$. This salt was prepared by a slight modification of the reported method.[9] The starting compound, $K_4Mo(CN)_8$, was obtained from a standard literature procedure.[10] $K_4Mo(CN)_8$ (4.0 mmol, 1.98 g) was dissolved in 8 mL of distilled water. Gradual addition of 10 mL of concentrated HNO_3 with constant stirring caused the yellow solution of Mo(IV) to turn dark brown and finally light yellow. This solution was diluted to 40 mL, followed by slow addition of 0.012 mol (2.85 mL) of tri-*n*-butylamine. No precipitate was observed in 6 min, but further dilution to 60 mL with water produced a light yellow precipitate. The precipitate was filtered, washed with water, and dried in a vacuum desiccator. Yield of $[HN(n\text{-}C_4H_9)_3]_3[Mo(CN)_8]$: 86.7%.

$[HN(n\text{-}C_4H_9)_3]_3[Mo(CN)_8]$ (2.2 mmol, 1.94 g) was dissolved in the minimum volume of methanol, ca. 25 mL. CsCl (1.2 g) was also dissolved in the minimum volume of methanol (100 mL) and added slowly into the yellow solution of $[HN(n\text{-}C_4H_9)_3]_3[Mo(CN)_8]$ with stirring, yielding a light yellow precipitate of $Cs_3Mo(CN)_8$. This powder was filtered, washed with cold water and methanol, and dried in a vacuum desiccator. Yield: 96%. Molar absorptivities of aqueous $[Mo(CN)_8]^{3-}$ solution determined by UV−vis spectra ($M^{-1}\ cm^{-1}$): 2.74×10^3 (254 nm), 2.83×10^3 (268 nm), and 1.46×10^3 (388 nm). These values are in good agreement with the reported values[7] and hence support the purity of this compound.

Methods. UV−vis spectra were recorded on a HP-8453 diode-array spectrophotometer equipped with a thermostated water bath to maintain the temperature at 25.0 ± 0.1 °C. A Corning pH meter, model 130, with a Mettler semimicro combination glass electrode was used for pH measurements.

Kinetic studies of slow reactions (pH < 6.5) were monitored on a HP-8453 spectrophotometer, with an attached RM6 Lauda circulatory water bath, using stoppered 1 cm quartz cuvettes. Fast reactions (pH > 6.75) were investigated on a Hi-Tech Scientific model SF-51 stopped-flow apparatus equipped with a SU-40 spectrophotometer unit in the 1.0 cm path length configuration and a C-400 circulatory water bath. Temperature was maintained at 25 ± 0.1 °C. Stopped-flow studies were performed by mixing equal volumes of the two reactants, both of which were maintained at 0.1 M ionic strength, and an OLIS 4300S system was used for data acquisition and analysis.

^1H NMR spectra of reactant and product solutions were performed with a Bruker AC 250 spectrometer.

Results

Metal-Ion Catalysis. Preliminary study of the reaction of excess thioglycolic acid with $Cs_3Mo(CN)_8$ showed that the reaction is fast at [TGA] = 5 mM, $[Mo(V)]_0 = 0.1$ mM, pH = 4.5, [NaOAc] = 0.02 M, and $\mu = 0.1$ M ($NaClO_4$). The decay curve at 388 nm was exponential with a rate constant of 1.1 s^{-1}. In the presence of 0.02 mM Cu^{2+} ion, the above reaction was much faster with the first half-life only 75 ms, which indicates that copper is a highly effective catalyst for the reaction. The same reaction with no added Cu^{2+} ion and in the presence of 1.0 mM 1,10-phenanthroline, as a chelating agent, was slow with a 35 s first half-life, and showed zero-order kinetics. Similar results were observed when other chelating agents were used, e.g., 2,2'-bipyridine, 5-chlorophenanthroline, 5-nitrophenanthroline, 4-methylphenanthroline, and 2,6-pyridinedicarboxylic acid (dipic). These results indicate that the reaction is catalyzed by metal ion impurities and that the catalysis can be effectively masked by these chelating agents. All further experiments were conducted in the presence of dipic in order to prevent catalysis by metal-ion impurities. Note that the prior study of the reaction of TGA with $[Mo(CN)_8]^{3-}$ makes no mention of the potential effects of metal-ion catalysis.[8]

Photochemical Effects. At pH 4.5 with 2 mM TGA, 80 μM Mo(V), and 1 mM dipic the reaction has a first half-life of about 200 s. In a series of experiments conducted under these conditions it was found that the light beam of the diode-array spectrophotometer (with both UV and vis sources on) has negligible photochemical effects. On the other hand, at pH 1.5 the reaction is much slower with a first half-life of about 4000 s (at 0.13 mM Mo(V)). Under these conditions a series of experiments showed that protecting the sample with a 375 nm optical cutoff filter placed in the beam path increased the first half-life from 3540 to 5000 s, and a further increase to 5500 s could be achieved by increasing the delay between spectra from 10 to 30 s (a shutter blocks the light beam between spectra). Alternatively, these photochemical

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effects could be eliminated by operating the instrument with only the visible source on. All further experiments with this instrument were conducted in this mode.

For the purpose of comparison with the prior study of this reaction by Olatunji and Okechukwu,[8] we investigated the reaction at 1 mM TGA and pH 1.79 (with 0.1 mM Mo(V) and 1 mM dipic at $\mu = 0.1$ M ($NaClO_4$)) and found that the reaction is very slow with a first half-life greater than 3000 s. A half-life of 1.5 s at this pH and TGA concentration can be inferred from the data in the prior report, in which no precautions were taken to prevent the effects of metal-ion catalysis or photolysis.[8] It is evident that the pseudo-first-order behavior and 1000-fold greater rate constants reported previously likely are artifacts arising from one or both of these effects.

Scavenger Effects. As noted above, at pH 2 the reaction is slow and occurs with kinetics intermediate between first and zero order, at pH ~4.5 the reaction is somewhat faster and zero order, and at pH 6.5 and 8.5 the reaction is much faster and first order. On the other hand, at pH 2 the addition of 1 mM PBN, a free-radical scavenger, leads to pseudo-first-order behavior and a moderate overall slowing of the reaction; increasing the PBN concentration to 5 mM has no further significant effect on the pseudo-first-order rate constants. Likewise at pH 4.5 the addition of PBN leads to first-order kinetics and an overall moderate slowing of the reaction. At pH 6.5 (phosphate buffer) with 4 mM TGA and no PBN the reaction is considerably faster than at pH 2 or 4.5, pseudo-first-order behavior is obtained, and the rate constants are insignificantly affected by the addition of 5 mM PBN. In order to obtain meaningful results below pH 6.5 and to maintain consistent conditions, all kinetic studies reported below were thus conducted in the presence of 2 mM PBN.

Stoichiometry and Product Characterization. Under typical conditions (excess TGA, added dipic and PBN), repetitive scans show that the reaction is characterized by a loss of absorbance in the UV due to the consumption of $[Mo(CN)_8]^{3-}$. The product mixture has a weak broad absorbance extending into the visible, which results in an isosbestic point at 427 nm.

The stoichiometry of the reaction in the presence of dipic and PBN was determined by spectrophotometric titration. A 2.5 mL portion of 1.0 mM deaerated TGA solution at 1.0 mM dipic, 2.0 mM PBN, 0.02 M carbonate buffer, and pH 11.0 was taken in a stoppered cuvette and titrated against 5 mM degassed Mo(V) solution. The absorbance was measured at 388 nm after addition of 0.1 mL increments of Mo(V) solution, yielding the titration plot shown in Figure 1. Before the end point is reached, the Mo(V) is consumed completely. At end point there is an abrupt change in slope due to the increase in absorbance as excess Mo(V) accumulates. Figure 1 indicates that the consumption ratio is 1.01 for $n_{Mo(V)}/n_{TGA}$, where n represents the number of moles of reactants. A similar experiment in the absence of PBN also yields a stoichiometric ratio of 1.0 for $n_{Mo(V)}/n_{TGA}$.

Products of the reaction were identified and quantitated by UV−vis and ^{1}H NMR methods. The molybdenum-containing product was characterized by UV−vis spectrophotometry. Samples of 0.1 mM Mo(V) solution were reduced with an excess of TGA at pH 6.0, 9.18, and 11.0, using 0.02 M phosphate, borate, and carbonate buffers, respectively. Spectra of the product solutions at all pH's were identical to that of an authentic $[Mo(CN)_8]^{4-}$ solution, which has a sharp peak at 241 nm; as inferred from the absorbance, the yield of Mo(IV) was 98 ± 5%. The identity of the sulfur-containing product was determined by ^{1}H NMR spectroscopy. ^{1}H NMR experiments performed under the conditions of [Mo(V)] = 10.0 mM, [TGA] = 50.0 mM, [dipic] = 5.0 mM at pH 6.56 and 10.20 in deaerated D_2O (with DSS as reference) clearly revealed the production of dithiodiglycolic acid by its resonance at 3.47 ppm (Figure 1-S, Supporting Information). Unlike for the reaction of TGA with $[IrCl_6]^{2-}$,[1] the NMR spectra obtained with $[Mo(CN)_8]^{3-}$ as oxidant provided no evidence for the production of the sulfonic acid. The above results imply that the overall reaction is

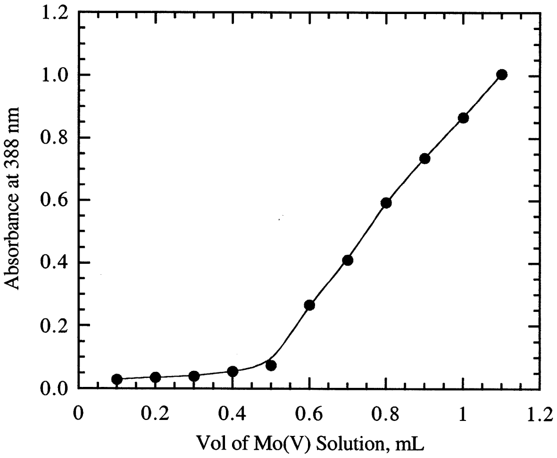

Figure 1. Absorbance at 388 nm vs volume of $[Mo(CN)_8]^{3-}$ solution for the spectrophotometric titration of 2.5 mL of 1.0 mM TGA solution at [PBN] = 2.0 mM, [dipic] = 1.0 mM, $\mu = 0.1$ M ($NaClO_4$), 0.02 M carbonate buffer, and pH = 11.0 against 5.0 mM Mo(V) solution.

$$2[Mo(CN)_8]^{3-} + 2HSCH_2COO^- \rightarrow 2[Mo(CN)_8]^{4-} + {}^-OOCCH_2SSCH_2COO^- + 2H^+ \quad (1)$$

Kinetics. The rate of reduction of $[Mo(CN)_8]^{3-}$ by TGA in the presence of 2 mM PBN and 1 mM dipic was investigated at 25 °C at various concentrations of reductant and from pH 1.7−12.0 at constant ionic strength ($\mu = 0.1$ M, $NaClO_4$). A first-order dependence of the rate on $[Mo(CN)_8]^{3-}$ was established by the linearity of plots of $-\log A_t$ vs t (where A_t is the absorbance at time t) over more than 3 half-lives. Pseudo-first-order rate constants (k_{obs}, s^{-1}) were evaluated by exponential fits of the kinetic curves, and replicate runs agreed to better than ±5%. Studies of the kinetic dependence on $[TGA]_{tot}$ were performed at pH 5.0 and 11.9, the results of which are given in Table 1-S (Supporting Information); here, $[TGA]_{tot}$ refers to the total concentration of TGA irrespective of its state of protonation. Plots of k_{obs} vs $[TGA]_{tot}$ (Figures 2-S and 3-S, Supporting

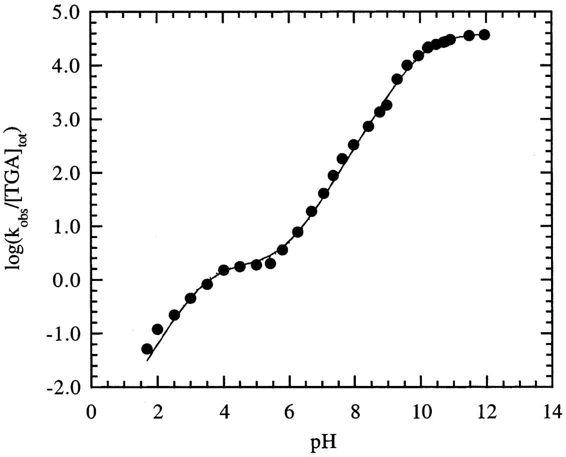

Figure 2. Log (k_{obs}/[TGA]$_{tot}$) vs pH for the reduction of $[Mo(CN)_8]^{3-}$ by thioglycolic acid at [Mo(V)] = 0.1−0.2 mM, [PBN] = 2.0 mM, [dipic] = 1.0 mM, μ = 0.1 M ($NaClO_4$), and temperature 25 °C. Reactions were carried out under anaerobic conditions. Calculated values are represented by the solid line, and experimental points are shown by solid circles (Table 2-S).

Information) are linear and pass through the origin, indicating a first-order dependence of rate on [TGA]$_{tot}$.

A complex pH dependence was revealed in a series of kinetic runs over the pH range 3.5−11.0, the values of k_{obs} being summarized in Table 2-S (Supporting Information). A plot of log(k_{obs}/[TGA]$_{tot}$) vs pH (Figure 2) shows that the rates increase dramatically with increasing pH and attain plateaus at pH ~5.0 and 11.0. This rate profile is clearly related to the two proton dissociation equilibrium constants[11−13] of TGA as follows.

$$HSCH_2COOH \rightleftharpoons HSCH_2COO^- + H^+ \qquad pK_{a1} = 3.53 \quad (2)$$

$$HSCH_2COO^- \rightleftharpoons {}^-SCH_2COO^- + H^+ \qquad pK_{a2} = 10.10 \quad (3)$$

For completeness we also consider the tautomerization equilibrium between $HSCH_2COO^-$ and $^-SCH_2COOH$ as shown in eq 4,

$$HSCH_2COO^- \rightleftharpoons {}^-SCH_2COOH \qquad K_i \qquad (4)$$

although the magnitude of K_i has not been reported. From the known values of pK_{a1} and pK_{a2} and the approximation that the two acidic groups do not interact with each other very strongly, a value of about 7 is predicted for pK_i, and hence equilibrium 4 should lie far to the left. A qualitative interpretation of the pH dependence in Figure 2 is that the thioglycolic acid molecule is essentially unreactive, and the singly deprotonated form of TGA is moderately reactive and leads to the plateau at pH 5, while the dianion is highly reactive and generates the plateau at pH 11.

A test for the effect of Mo(IV) was performed under the conditions of $[Mo(V)]_0$ = 0.1 mM, pH = 9.5, μ = 0.1 M ($NaClO_4$) and in the presence of 0.2 mM Mo(IV), but no evidence for kinetic inhibition was noted.

A rate law based on the above data and interpretation is

$$k_{obs} = \frac{XK_{a1}/[H^+] + YK_{a1}K_{a2}/[H^+]^2}{1 + K_{a1}/[H^+] + K_{a1}K_{a2}/[H^+]^2}[TGA]_{tot} \qquad (5)$$

A nonlinear least-squares fit of eq 5 with all the experimental data (Tables 1-S and 2-S) provides evaluated parameters of $X = 1.9 \pm 0.1$ M^{-1} s^{-1} and $Y = (3.70 \pm 0.14) \times 10^4$ M^{-1} s^{-1}. The excellent quality of the fit is demonstrated in Figure 2 by the overlap of the calculated solid line and the experimental data points (solid circles).

It is fairly common for reactions between $[Mo(CN)_8]^{3-}$ and anions to have rate laws that are first order in redox-inert cations such as the alkali metals. The oxidations of asrenite, sulfite, and thiosulfate are examples of this behavior.[5,6,14] We have not attempted to resolve this potential feature of the current rate law, but this omission should not introduce spurious terms in the rate law since the predominant cation in all of our experiments is always the same, Na^+. Any such catalytic effects should simply be included in the values of X and Y reported above.

Discussion

The reaction of TGA with $[Mo(CN)_8]^{3-}$ has several important qualitative points of comparison with the reaction of TGA with $[IrCl_6]^{2-}$.[1] Points of similarity include the high susceptibility to copper catalysis, the general form of the rate law for the uncatalyzed reaction, and the net one-electron reduction of metal complex without any perturbation to its coordination sphere. An important point of difference is in the overall stoichiometry, where the reaction of $[Mo(CN)_8]^{3-}$ yields the disulfide exclusively but the reaction of $[IrCl_6]^{2-}$ yields a mixture of the disulfide and the sulfonic acid. Another difference is the requirement for PBN in order for the reaction of $[Mo(CN)_8]^{3-}$ to obey pseudo-first-order kinetics in acidic media. This requirement for PBN probably arises from the relative slowness of the $[Mo(CN)_8]^{3-}$ reaction, which renders it more susceptible to short-chain reactions involving free-radical intermediates. PBN, a known free-radical spin trap, presumably functions in the present system by terminating these short-chain reactions. In view of the above, it is reasonable to propose that the main uncatalyzed reaction of TGA with $[Mo(CN)_8]^{3-}$ has the same mechanism as for the $[IrCl_6]^{2-}$ reaction, except for some of the post-rate-limiting steps.

One likely mechanism consists of the acid/base equilibria given in reactions 2−4 plus the following steps:

$$HSCH_2COO^- + [Mo(CN)_8]^{3-} \rightarrow [Mo(CN)_8]^{4-} + {}^{\bullet}SCH_2COO^- + H^+ \qquad k_a \quad (6)$$

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$$^{-}\mathrm{SCH_2COOH} + [\mathrm{Mo(CN)_8}]^{3-} \rightarrow [\mathrm{Mo(CN)_8}]^{4-} + {}^{\bullet}\mathrm{SCH_2COOH} \quad k_\mathrm{b} \tag{7}$$

$$^{-}\mathrm{SCH_2COO^-} + [\mathrm{Mo(CN)_8}]^{3-} \rightarrow [\mathrm{Mo(CN)_8}]^{4-} + {}^{\bullet}\mathrm{SCH_2COO^-} \quad k_\mathrm{c} \tag{8}$$

$$\mathrm{RS}^{\bullet} + \mathrm{RSH} \rightleftharpoons \mathrm{RSSR}^{\bullet -} + \mathrm{H}^+ \quad K_\mathrm{eq}, k_1, k_{-1} \tag{9}$$

$$\mathrm{RSSR}^{\bullet -} + [\mathrm{Mo(CN)_8}]^{3-} \rightarrow [\mathrm{Mo(CN)_8}]^{4-} + \mathrm{RSSR} \quad k_2 \tag{10}$$

The mechanism proposed for the $[IrCl_6]^{2-}$ reaction includes a series of additional steps that lead to RSO_3^- by direct oxidation of $RS^{\bullet}$.[1] It is reasonable to omit this pathway in the reaction with $[Mo(CN)_8]^{3-}$ because this oxidant is weaker than $[IrCl_6]^{2-}$, and therefore the rate of direct oxidation of $RS^{\bullet}$ should be slower and less able to compete with steps 9 and 10. Another route to the disulfide product could be important at low pH where reaction 9 is shifted to the left, and this is the dimerization of $RS^{\bullet}$; for simplicity we omit this possibility, although its inclusion would not drastically affect the rate law.

An estimate of the driving force for reaction 8 can be obtained from the standard potentials of the respective redox couples. The $E°$ value of the $^{-}SCH_2COO^-/{}^{\bullet}SCH_2COO^-$ couple has been calculated by combining eq 3 (K_{a2}) and eq 11.[15] This $E°'$ value was calculated from the ΔE of TGA

$$\mathrm{H}^+ + {}^{\bullet}\mathrm{SCH_2COO^-} + \mathrm{e}^- \rightleftharpoons \mathrm{HSCH_2COO^-} \quad E°' = 1.34\ \mathrm{V} \tag{11}$$

relative to the ClPz half-reaction considering the potential of the $ClPz^{2+/+}$ couple to be 0.83 V.[16] From the relation $E° = E°' + 0.059(\log K_{a2})$, we calculate that $E°$ of the $^{-}SCH_2COO^-/{}^{\bullet}SCH_2COO^-$ couple is 0.735 V. With the $E°$ value of the $[Mo(CN)_8]^{3-/4-}$ couple at 0.1 M ionic strength in hand (0.751 V),[17] we obtain a value of 1.86 for the equilibrium constant of reaction 8. Since this value is not highly unfavorable and the product radical is rapidly scavenged, it is reasonable to treat reaction 8 as an irreversible process in deriving a rate law from this mechanism.

With the steady-state approximation made for $[RS^{\bullet}]$ and $[RSSR^{\bullet -}]$, the above mechanism leads to

$$-\frac{\mathrm{d[Mo(V)]}}{\mathrm{d}t} = \frac{2\{(K_{a1}k_a + K_{a1}k_bK_i)[\mathrm{H}^+] + k_cK_{a1}K_{a2}\}}{[\mathrm{H}^+]^2 + K_{a1}[\mathrm{H}^+] + K_{a1}K_{a2}}[\mathrm{Mo(V)}][\mathrm{RSH}]_{\mathrm{tot}} \tag{12}$$

Comparison of eq 12 with the observed rate law, eq 5, shows that the two are equivalent and establishes values of 0.95 ± 0.05 $M^{-1}\ s^{-1}$ and $(1.85 \pm 0.07) \times 10^4\ M^{-1}\ s^{-1}$ for $(k_a + k_bK_i)$ and k_c, respectively.

Some further comment on the role of PBN relates to its potential effect on the stoichiometry. We first note that the stoichiometry measurements were performed at relatively high pH, and at this pH PBN has no significant kinetic effect. If the role of PBN at lower pH is to terminate short-chain radical side reactions, then it should have no effect on the stoichiometry. If it is more centrally involved in the mechanism and scavenges virtually all the $RS^{\bullet}$ radicals, then the overall reaction could be

$$[\mathrm{Mo(CN)_8}]^{3-} + \mathrm{TGA} + \mathrm{PBN} \rightarrow [\mathrm{Mo(CN)_8}]^{4-} + \mathrm{TGA{-}PBN}^{\bullet} \tag{13}$$

In this case the $\Delta[Mo(V)]/\Delta[TGA]$ ratio would still be 1:1. We have previously reported evidence that the $N_3^{\bullet}$/DMPO spin adduct is oxidized by $[IrCl_6]^{2-}$,[18] and that the $N_3^{\bullet}$/PBN spin adduct is not oxidized by ClO_2.[19] As the observed stoichiometry in the present reaction is 1:1 both with and without PBN, these measurements provide no information relating to the mechanistic role of PBN. Further study on the oxidation of spin adducts could be informative.

Marcus Theory. Analysis of the rates at intermediate pH values is problematic because of the kinetic proton ambiguity relating to tautomerization of the TGA monoanion. On the other hand, at high pH the k_c rate constant is unambiguously resolved and is discussed in greater detail.

An outer-sphere electron-transfer mechanism is suggested for this step (oxidation of the TGA dianion, reaction 8) by the fact that the coordination sphere of the Mo-containing product is not altered by the overall redox reaction. Moreover, no inner-sphere species was detected as a transient during the reaction. An outer-sphere mechanism can also be anticipated because $[Mo(CN)_8]^{3-}$ is often found to react in this way.[3,20,21] On the other hand, an inner-sphere mechanism in which a weak (CN)−S link exists in the transition state cannot be completely excluded; the basis for this suggestion is the reports that $[Fe(CN)_6]^{3-}$ reacts with $SO_3^{\bullet -}$ and RS^- to form a similar (CN)−S linkage.[22,23] Irrespective of this consideration, this appears to be only the second report of the kinetics of oxidation of an aliphatic thiol by a classical “outer-sphere” oxidant that is uncompromised by potential copper catalysis.

In view of the possibility that the k_c rate constant corresponds to a genuine outer-sphere electron-transfer process, it is of interest to explore the application of the cross relationship of Marcus theory. In order to compare the results with those obtained for the oxidation of TGA by $[IrCl_6]^{2-}$ it is necessary to include work terms to account for the differing charges of the two oxidants. Thus, the form of the cross relationship to be used is given by

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$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{14}$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT]} \tag{15}$$

$$W_{12} = \exp[(-w_{12} - w_{21} + w_{11} + w_{22})/2RT] \tag{16}$$

$$w_{ij} = 4.23Z_iZ_j/[a(1 + 0.328a\sqrt{\mu})] \tag{17}$$

where k_{12} is the observed cross electron-transfer rate constant, k_c, and k_{11} and k_{22} are the self-exchange rate constants of the $[Mo(CN)_8]^{3-/4-}$ and $^{-}SCH_2COO^{-}/^{\bullet}SCH_2COO^{-}$ redox couples.[24] We use a value for k_{11} of 3.0×10^4 M^{-1} s^{-1}.[20] Z is the collision frequency for which we use a value 1.0×10^{11} M^{-1} s^{-1}. Z_i and Z_j are the ionic charges on the reactants, R is the universal gas constant (1.98×10^{-3} kcal mol^{-1}), and a is the center to center distance (Å) when the reactants are in contact. The radius of $[Mo(CN)_8]^{3-}$ (4.7 Å) is obtained from the radius of $[Fe(CN)_6]^{3-}$ (4.1 Å) by correction for the difference in ionic radius between Fe^{3+} (0.69 Å) and Mo(V) (0.75 Å). The radius of 2.6 Å for $^{-}SCH_2COO^{-}$ was approximated from its CPK model.[1]

With the above parameters, the value of K_{12} calculated above (1.86), and the experimental value of k_{12}, iterative solution of eqs 14−17 yields a value of 2.8×10^3 M^{-1} s^{-1} for k_{22}, the effective $^{-}SCH_2COO^{-}/^{\bullet}SCH_2COO^{-}$ self-exchange rate constant. This result is lower than the k_{22} value of 1.5×10^5 M^{-1} s^{-1}, which was derived from the reaction of $[IrCl_6]^{2-}$ with TGA. However, considering the high charges involved, the potential catalytic effects of "inert" cations, and the tendency of this method to magnify errors, the results may be regarded as consistent with an outer-sphere electron-transfer mechanism for the oxidation of the TGA dianion by both $[Mo(CN)_8]^{3-}$ and $[IrCl_6]^{2-}$.

Acknowledgment. This research was supported by a grant from the NSF.

Supporting Information Available: Listings of pseudo-first-order rate constants, ^{1}H NMR spectrum of product solution, and plots of k_{obs} as a function of $[TGA]_{tot}$. This information is available free of charge via the Internet at http://pubs.acs.org.

IC025702Z

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