

# Oxidation of Polyvinyl Mercaptan and Related Model Compounds by Molecular Oxygen<sup>1</sup>

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*The autoxidation of a series of dithiols and polyvinyl mercaptan has been studied kinetically by volumetric measurement of the oxygen consumption. A variety of catalysts in aprotic solvents were examined, and ferric sulfate in dimethyl sulfoxide was selected as the system most consistently producing disulfide as the only oxidation product. The oxidation rate was directly proportional to the iron concentration and was sensitive to the structure of the thiol substrate. A mechanism is proposed which involves an oxidation-reduction reaction between a ferric and ferrous thiol complex as the intermediary between oxygen and thiol. Proximity effects of the neighboring mercapto functions and polymer effects were observed.*

## Introduction

Interest in mercaptan oxidation stems from the biological significance of the sulfhydryl group, the potential application of mercaptoamino compounds as radiation prophylactics, and the feasibility of removing undesirable mercaptan impurities from petroleum by oxidative processes. Although the mechanism and stoichiometry of mercaptan oxidation are dependent upon the nature of the catalyst employed, systems which duplicate the physiological stoichiometry,  $4\text{RSH} + \text{O}_2 = 2\text{RSSR} + 2\text{H}_2\text{O}$ , have received the most attention. Working with aqueous solutions of glutathione, cysteine, and thioglycolic acids, early investigators found that oxidation of thiols to disulfides by molecular oxygen required the presence of an electroactive oxidation-reduction mediator.<sup>4</sup> This mediator, usually a transition metal, would function either as a catalyst or as an inhibitor depending upon the complexing ability of the thiol, the oxidation-reduction potential of the complex formed, and the ionic environment in which the oxidation occurred. Kinetic studies on transition metal-aqueous oxidizing systems have been carried out manometrically<sup>5</sup> and spectrophotometrically,<sup>6</sup> and variables such as dithiol proximity,

neighboring group effects, and pH have been investigated.

The oxidation of thiols in alkaline media is considerably more complex. Xan, *et al.*,<sup>7</sup> studied a series of mercaptans in aqueous sodium hydroxide solutions and observed oxygen uptakes exceeding the theoretical consumption expected if 4 moles of thiol were being oxidized by 1 mole of oxygen. Recently this observation was shown to be due to formation of sulfinic and sulfonic acids.<sup>8,9</sup> In a detailed investigation of *n*-octyl mercaptan oxidation in *t*-butyl alcohol in the presence of potassium *t*-butoxide, Berger found that disulfide formation predominated at low base concentrations, but the extent of acid formation increased rapidly as the concentration of base increased. The author proposed that un-ionized mercaptan produced disulfides while ionized mercaptan was oxidized further to sulfinic and sulfonic acids by a complex scheme involving direct addition of O<sub>2</sub> to the mercaptan anion. The product distribution appeared to be a function of the degree of dissociation of the mercaptan.

Support for this hypothesis can be found in the relative oxidation rates observed in a series of aprotic solvents of increasing polarity.<sup>10</sup> Although the products were not identified, the maximum rate of oxygen uptake during the oxidation of *n*-butyl mercaptan in the presence of excess sodium methoxide occurred in dimethylformamide, a solvent which promotes anionic reactions. In a subsequent publication<sup>9</sup> the same authors showed that 1-butanefulfonic acid was the principle product under these oxidative conditions and suggested initial oxidation of the butanethiol to the disulfide followed by nucleophilic attack on the disulfide linkage by hydroxyl anion to produce a mercaptide ion and a sulfenate ion. The sulfenate ion then disproportionates to the corresponding sulfonic acid and disulfide.

Although the authors did not agree on the precise mechanism, from their results it was clear that the overall stoichiometry of the reaction is complicated by the concurrent formation of disulfide, sulfinic acid, and sulfonic acid. Therefore, measurement of oxygen uptake does not define the oxidation rate unless the relative yields of the various products are determined.

A technique for following the rate of oxidation of thiols by 2,6-dichlorophenolindophenol spectrophotometrically was developed by Basford and Huennekens.<sup>11</sup> In order to determine the relative rates of oxidation of

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(2) NATO Postdoctoral Fellow, 1963-1964.

(3) This paper comprises a portion of a dissertation submitted by W. H. Daly in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the graduate school of the Polytechnic Institute of Brooklyn.

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polymercaptans and their corresponding model compounds, this procedure was modified for use in pH 10 aqueous buffer solution<sup>12</sup> and in organic solvents.<sup>18</sup> In the pH 10 buffer systems, a proximity effect was illustrated by the enhanced oxidation rates of 2,4-di(*p*-mercaptophenyl)pentane and poly(*p*-mercaptostyrene) over *p*-thiocresol. Only a slight increase in the ease of oxidation of the polymers in comparison with their model compounds was observed. However, the proximity effect of neighboring sulfhydryl substituents became pronounced when the oxidation was carried out in dimethylformamide. The results obtained for polyvinyl mercaptan and a series of dithiols are summarized in Table I.

Table I.<sup>18</sup> Relative Oxidation Rates of Thiols in DMF

Thiol	Observed oxidation rates, mole ml. <sup>-1</sup> min. <sup>-1</sup> × 10 <sup>6</sup> <sup>a</sup>	Relative rates
2,6-Heptanedithiol	0.328	1.0
2,5-Hexanedithiol	3.90	11.9
2,4-Pentanedithiol	9.70	28.7
2,3-Butanedithiol	20.1	61.2
Poly(vinyl mercaptan)	91.4	280

<sup>a</sup> On the basis of one SH group oxidized.

The tenfold increase in the oxidation rate of polyvinyl mercaptan over 2,5-pentanedithiol was indicative of a "polymer effect" and warranted further investigation. In view of the recent discovery that the addition of mercaptans to 2,6-dichlorophenolindophenol is occurring concurrently with the anticipated reduction,<sup>14</sup> the selection of another oxidation technique was imperative.

## Experimental

**Reagents.** Dimethyl sulfoxide (DMSO) was treated with Dowex chelating resin A-1 to remove trace metal ions and distilled in a nitrogen atmosphere under reduced pressure, b.p. 88° (24 mm.), *n*<sup>20</sup><sub>D</sub> 1.4793.

Spectroquality reagent grade dimethylformamide (DMF) was used without further purification.

Ferric sulfate stock solutions were prepared by dissolving 1.25 g. of hydrated ferric sulfate in 50 ml. of DMSO. Heating to 70° for 3 hr. was required to obtain clear solutions. The iron concentration was determined potentiometrically<sup>15</sup> and catalyst solutions were prepared by dilution.

The dithiols were prepared from the corresponding dibromides *via* the diisothiuronium salts<sup>13</sup> and purified by fractional distillation under reduced pressure. Dithiols of the following purity were used: 2,4-pentanedithiol, b.p. 67° (12 mm.), *n*<sup>18</sup><sub>D</sub> 1.5060 (lit.<sup>13a</sup> b.p. 65.5–67° (13 mm.), *n*<sup>18</sup><sub>D</sub> 1.5061); 2,5-hexanedithiol, b.p. 87–88° (11 mm.), *n*<sup>18</sup><sub>D</sub> 1.5050 (lit.<sup>13a</sup> b.p. 87–88°

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(11 mm.), *n*<sup>18</sup><sub>D</sub> 1.5051); 2,6-heptanedithiol, b.p. 101° (11 mm.), *n*<sup>26</sup><sub>D</sub> 1.4975 (lit.<sup>13b</sup> b.p. 120° (26 mm.), *n*<sup>25</sup><sub>D</sub> 1.4978).

**Polyvinyl Mercaptan.** S-Vinyl-O-*t*-butyl thiolcarbonate was prepared by treating S-(β-chloroethyl) chlorothiolformate with potassium *t*-butoxide and was polymerized in the presence of azobisisobutyronitrile.<sup>1b</sup> The polymer, 2.0 g., was dissolved in a mixture of 20 ml. of tetrachloroethane and 70 ml. of chloroform and treated with anhydrous hydrogen bromide for 4 hr. The chloroform was evaporated *in vacuo* and the polymercaptan was precipitated by addition of the tetrachloroethane solution to methanol. The polymer was reprecipitated from 15 ml. of DMSO into a 2:1 methanol-pentane mixture and dissolved in DMSO, and the solution was diluted to 50 ml. in a volumetric flask. All operations were carried out under nitrogen in a glove bag.

A 2-ml. aliquot of the solution was titrated immediately using the HgCl<sub>2</sub>-DMSO-KOH technique (to be described below), and the mercaptan content was found to be 0.210 mequiv./ml. (84%). Additional assays 16 and 36 hr. later yielded values of 0.208 and 0.205 mequiv./ml., respectively, indicating that oxidation of polyvinyl mercaptan by DMSO at 30° is negligible.

**Determination of Sulfhydryl Assay.** The following modification of the procedure given by Overberger<sup>18</sup> was used. Solutions containing 6 g. of mercuric chloride in 300 ml. of DMSO and 26 g. of sodium chloride in 1 l. of water were prepared. An aliquot of mercaptan solution containing 0.1 to 0.5 mequiv. of thiol was added to 20 ml. of the mercuric chloride solution and stirred for at least 30 min. This mercaptide solution was stable and could be allowed to stand for several hours without influencing the titration. Immediately prior to titration, 150 ml. of sodium chloride solution was added to the solution and the mixture was titrated potentiometrically with 0.1 *N* potassium hydroxide. The procedure was equally as effective for polyvinyl mercaptan as for the dithiols, despite the fact that the polymercaptide precipitated immediately upon addition of the aliquot to the mercuric chloride solution.

**Kinetic Procedure.** The gas measuring unit consisted of a water jacketed gas buret and reference tube which were coupled by a manometer. The buret was connected to a leveling bulb and both were filled with triacetin. At the beginning of each run the buret was flushed once and then filled with oxygen, which was passed through a drying tower filled with Drierite and used without further purification. The required volume of solvent was added to an erlenmeyer flask equipped with side arm and stirring bar. The flask was immersed in a constant temperature bath and was connected to the gas buret with 1-mm. capillary tubing. The reaction vessel was flushed with oxygen for 10 min. while coming to equilibrium with the constant temperature bath. The side arm was sealed with a serum cap and stirring was initiated. After the solvent was saturated with oxygen the system was checked to ensure that no oxygen uptake was occurring. The stirring was stopped and the polymercaptan solution was injected with a hypodermic syringe. The stirring was restarted and the rate of oxygen uptake catalyzed by adventitious metal ions was recorded to make sure

it was not excessive. The stirring was stopped again while the catalyst solution was injected. Finally the stirring was restarted and the volume of gas absorbed was recorded at fixed intervals (usually every 0.5 min.). The beginning of stirring was considered time zero. Rapid stirring was used to obtain reaction rates independent of the rate of agitation. It was assumed this independence signified that the rate of oxygen diffusion into the solution did not affect the oxidation rate.

The change in mercaptan concentration was calculated from the volume of oxygen consumed by the following equation

$$C_{\text{SHR}} = \frac{273(4)(1000)(PV_{\text{ox}})}{760(22415)(TV_{\text{sol}})}$$

$$= 0.64101 \frac{PV_{\text{ox}}}{TV_{\text{sol}}}$$

where  $C_{\text{SHR}}$  = concentration of mercaptan reacted in mole/l.,  $T$  = temperature of the water jacket in °K.,  $P$  = atmospheric pressure,  $V_{\text{ox}}$  = milliliters of oxygen absorbed, and  $V_{\text{sol}}$  = milliliters of the reaction mixture. The initial concentration was calculated from the SH titer of the stock solution. Subtraction of  $C_{\text{SHR}}$  from the initial concentration gave the mercaptan concentration ( $C_{\text{SHT}}$ ) at the time the reading was taken. A plot of  $C_{\text{SHT}}$  vs. time was a straight line with a slope equal to the rate of the reaction. All calculations including a least-square evaluation of the slope were done by an IBM 7040 computer.

In experiments where the per cent reaction calculated from the oxygen uptake was compared with per cent reaction calculated from mercaptan consumption, an aliquot was withdrawn from the reaction vessel with a hypodermic syringe and added to 20 ml. of mercuric chloride solution. The hydrogen chloride liberated was titrated as previously described. The aliquots were withdrawn before precipitation of the polymer, due to cross linking by disulfide formation, had occurred.

**Ultraviolet Experiments.** A Bausch and Lomb Spectronic 505 spectrophotometer equipped with external recorder was used to follow changes in optical density at a given wave length with time. The reference cell always contained pure dimethyl sulfoxide. The sample cell was filled with mercaptan solution and was stoppered with a serum cap. The solution was saturated with either oxygen or nitrogen using hypodermic needles to achieve an effective stream of gas through the liquid. Then the catalyst solution was injected with a microsyringe. The cell was shaken to mix the reactants and measurement was begun as soon as possible. The maximum absorbance of the ferric-thiol complex was shown to follow Beer's law.

## Results

**Selection of an Oxidizing System.** After examining the various oxidants reported for mercaptans, molecular oxygen was chosen as the most suitable for kinetic study. The use of a gaseous reactant would minimize problems inherent to polymeric substrates such as consumption of oxidant by selective absorption or variations in local concentrations of reactants due to ineffective dispersion in viscous media.<sup>16</sup> Thus it was

(16) The question of selective absorption of 2,6-dichlorophenolindophenol by the polymer in the previous oxidation studies had not been adequately clarified. Since these measurements were based on the dis-

necessary to find a solvent for both monomeric and polymeric mercaptans which would not react with oxygen, catalyst, or thiol, and a catalyst which induced only disulfide formation *via* a simple stoichiometric reaction. In addition, an oxidizing system which was sensitive to the structure of the substrate was required.

Anchimeric assistance by sulfhydryl anions had been postulated to explain the proximity effect on the oxidation rate of dithiols and polymercaptans. Therefore, reactions involving the ionization of the sulfhydryl group were expected to be influenced by the structure and possibly the stereochemistry of the mercaptan. A survey of solvent catalyst systems indicated that potassium hydroxide in aqueous dimethylformamide would be compatible with both polymeric and monomeric thiols.

When preliminary volumetric measurements of oxygen consumption by dithiols in the presence of base were compared with titrations of residual dithiol in the oxidized solution, it was apparent that the reaction was proceeding beyond the disulfide oxidation state. Polyvinyl mercaptan did not precipitate during the oxidation as would be expected if cross-linking *via* disulfide formation were occurring. However, 2,5-hexane disulfide did not absorb oxygen when treated under the same conditions used to oxidize the corresponding dithiol. These results appear to confirm the direct oxidation of mercaptan anion to sulfonic and sulfinic acids as proposed by Berger.

The oxidation of dithiols in the presence of base was further complicated by the neutralization of catalyst by the sulfinic and sulfonic acids formed and by alkaline hydrolysis of dimethylformamide. Addition of potassium hydroxide to 90% aqueous DMF and stirring for periods of time varying up to 15 min. resulted in significant reductions in the initial oxidation rates. Although the consumption of catalyst by hydrolysis of DMF could be eliminated by employing dimethyl sulfoxide as the solvent, the base was neutralized so rapidly by the acid formation that meaningful initial rates could not be obtained.

Since transition metal catalysts in aqueous systems had been successfully employed in kinetic studies of mercaptan oxidation,<sup>17</sup> the possibility of their use in polar aprotic solvents was investigated. Hemin was briefly examined as a catalyst, but the oxidation exhibited a long induction time in DMF and copper phthalocyanine in DMSO did not catalyze the oxidation. Although colored complexes formed, they appeared to be too stable to act as catalysts.

Two satisfactory systems involving ferric ions were found: ferric chloride in DMF and ferric sulfate in DMSO. The DMSO-ferric sulfate system was preferred because DMF was subject to hydrolysis in acidic media. The DMSO did not react with oxygen and did not catalyze the oxygen uptake by dithiols. The oxidation of aliphatic mercaptans at high temperatures by DMSO to the corresponding disulfides has been reported,<sup>18</sup> but periodic titration of dithiol solu-

appearance of the dye, it is conceivable that absorption processes contributed to the enhanced oxidation rates observed for polyvinyl mercaptan in DMF.

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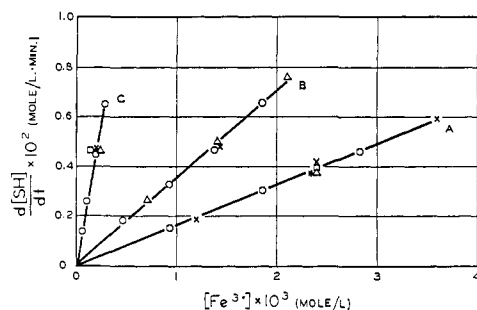


Figure 1. Effect of ferric sulfate concentration on rate of oxidation at various mercaptan concentrations in DMSO. (A) 2,6-Heptanedithiol concentrations in moles of SH/l.:  $\times$ , 0.824 mole/l.;  $\circ$ , 0.3595 mole/l.;  $\triangle$ , 0.0912 mole/l.;  $\square$ , 0.3649 mole/l.;  $*$ , 0.7190 mole/l. (B) 2,5-Hexanedithiol concentrations in moles SH/l.:  $\circ$ , 0.1885 mole/l.;  $\times$ , 0.7429 mole/l.;  $\triangle$ , 0.3714 mole/l. (C) 2,4-Pentanedithiol concentrations in moles SH/l.:  $\circ$ , 0.0384 mole/l.;  $\triangle$ , 0.0768 mole/l.;  $\square$ , 0.1152 mole/l.;  $\times$ , 0.1919 mole/l.

tions stored at 30° indicated that the oxidation rate was negligible at this temperature. Since all oxidation experiments were carried out at 30°, no appreciable oxidation of mercaptan by DMSO was expected.

*Autoxidation in the Dimethyl Sulfoxide-Ferric Sulfate System.* The relative oxidation rates of 2,6-heptanedithiol, 2,5-hexanedithiol, 2,4-pentanedithiol, and polyvinyl mercaptan were measured in DMSO in the presence of ferric sulfate. Using the stoichiometry  $4SH + O_2 \rightarrow 2RSSR + 2H_2O$ , the mercaptan concentration was calculated from oxygen uptake and compared with the mercaptan titer of aliquots withdrawn from the oxidizing reaction mixture. The data in Table II indicate that the anticipated stoichiometry is valid for the initial 20% of reaction.

Table II. Comparison of Per Cent Reaction Calculated from Oxygen Uptake and Mercaptan Titration

Compd.	[SH], mole/l.	[Fe <sup>3+</sup> ], mole/l. $\times 10^3$	Initial rate $\times 10^3$	Reaction, % Oxygen uptake	Titration
Poly(vinyl mercaptan)	0.021	0.025	0.73	9.3	10.1
	0.021	0.025	0.68	16.5	15.8
	0.021	0.025	0.69	22.1	23.5
	0.021	0.025	0.72	37.2	30.0
2,5-Hexanedithiol	0.371	0.703	2.75	5.0	4.6
	0.371	1.406	4.95	9.9	9.9
	0.371	2.109	7.66	11.8	12.0
	0.188	2.310	...	27.5	30.5
2,6-Heptanedithiol	0.182	1.198	1.90	9.1	9.4
	0.182	2.396	4.05	18.8	18.5
	0.182	3.593	5.93	28.3	24.5
	0.182	4.791	8.40	36.5	30.0

When a sufficient excess of mercaptan over ferric sulfate was employed the mercaptan concentration decreased linearly with time, establishing pseudo-zero-order kinetics in mercaptan. The initial slope of this graph was considered the oxidation rate. No induction period was observed, indicating that the time required for formation of the ferric-thiol complex could be considered negligible in comparison with the period of measurement. A log-log plot of the oxidation rates vs. iron(III) concentration showed that the reaction is first order with respect to iron(III). Figure 1 illustrates the reaction rates obtained for a series of

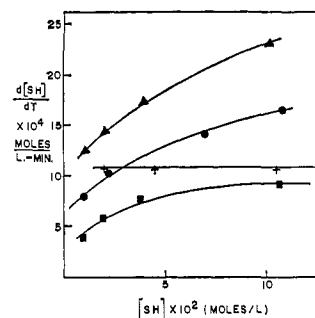


Figure 2. Effect of mercaptan concentration on oxidation rate at iron concentrations. Pentanedithiol [Fe<sup>3+</sup>]:  $+$ ,  $0.032 \times 10^{-3}$  mole/l. Poly(vinyl mercaptan) [Fe<sup>3+</sup>]:  $\blacksquare$ ,  $0.016 \times 10^{-3}$  mole/l.;  $\bullet$ ,  $0.032 \times 10^{-3}$  mole/l.;  $\blacktriangle$ ,  $0.047 \times 10^{-3}$  mole/l.

dithiols and demonstrates the independence of the oxidation rate on dithiol when the concentration is varied from 0.02 to 0.35 mole/l. at constant iron(III) concentrations. A similar, first-order dependence on ferric sulfate concentration was observed for the polyvinyl mercaptan oxidation, but as is shown in Figure 2 a dependency on mercaptan concentration was also found. The average order of reaction with respect to polymercaptan was estimated to be 0.3 from the slope of a log-log rate vs. mercaptan plot.

*Ultraviolet Elucidation of Mechanism.* A study of the ultraviolet spectra of the ferric-thiol complex was conducted to further elucidate the mechanism of oxidation. The complexes exhibited absorption maxima around 350 and 520 m $\mu$  (Table III).

Table III. Principle Ultraviolet Absorbances ( $m\mu$ ) of Thiol-Ferric Complexes<sup>a</sup>

Compd.	Ferric complex	Disulfide
Poly(vinyl mercaptan)	485, 335	330
2,4-Pentanedithiol	494, 350	345
2,5-Hexanedithiol	532, 360	286
2,6-Heptanedithiol	516, 362	...

<sup>a</sup> Solvent, dimethyl sulfoxide; catalyst, ferric sulfate.

The absorption in the 520-m $\mu$  region was selected for rate measurements so that interference by the disulfide absorption at lower wave lengths would be avoided. The characteristic behavior of the ferric-thiol complex under nitrogen and oxygen is plotted in Figure 3. Following a short induction period during which the complex is formed, the complex is reduced rapidly in the absence of oxygen. Subsequent treatment with oxygen regenerates the active species, indicating that an oxidation-reduction reaction between a ferric-ferrous thiol complex is the intermediary for the oxidation of mercaptans by molecular oxygen. Under oxygen the ferric-thiol complex concentration remains constant, suggesting that every step following the complex reduction is faster than the reduction reaction. Thus the reduction of the ferric complex appears to be the rate-determining step. Further ultraviolet investigation showed that the mercaptan concentration influenced the rate of complex formation and reduction when the mercaptan and iron concentrations were in the same order of magnitude. These

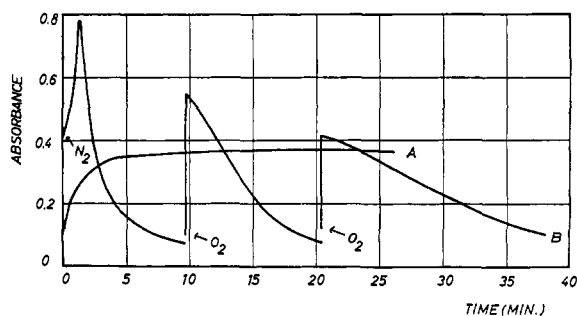


Figure 3. Change of absorbance at 532  $m\mu$  with time for the ferric complex of 2,5-hexanedithiol in DMSO. (A) (under oxygen):  $[SH] = 93.6 \times 10^{-8}$  mole/l.;  $[Fe^{3+}] = 0.951 \times 10^{-3}$  mole/l. (B) (under nitrogen, with regeneration of ferric complex by treatment with oxygen for 30 sec.):  $[SH] = 93.6 \times 10^{-8}$  mole/l.;  $[Fe^{3+}] = 1.841 \times 10^{-3}$  mole/l.

observations demonstrated that a mercaptan molecule was involved in the rate-determining step although pseudo-zero-order dependency was found at higher mercaptan to iron ratios. A similar change in order was observed in the reaction of 2,2-diphenyl-1-picrylhydrazyl with *t*-butyl hydroperoxide as the hydroperoxide concentration was increased.<sup>19</sup>

Lamfrom and Nielson<sup>6b</sup> have postulated short-lived free radicals as intermediates in the iron-catalyzed oxidation of thioglycolate. The reduction of the ferric-thiol complex under nitrogen was conducted in the presence of 2,2-diphenyl-1-picrylhydrazyl (DPPH), an efficient radical scavenger, in an attempt to provide better evidence for this postulation. Since DPPH is reduced by the sulphhydryl group,<sup>20</sup> it was necessary to study the relationship between the reduction of DPPH by a mixture of mercaptan and ferric-thiol complex under oxygen and the reduction by pure mercaptan. Figure 4 illustrates that DPPH does not react with ferric sulfate under oxygen and that the reaction with dithiol alone is ten times slower than in the presence of the iron(III) catalyst. Interpretation of this observation is complicated by the report that DPPH is quantitatively reduced by ferrous ions.<sup>21</sup> However, considering the rapid reaction of the ferrous-thiol complex with oxygen and the 100-fold excess of oxygen over DPPH, reaction of the iron(II) complex with DPPH probably would not produce a rate increase of the magnitude observed. The enhanced reduction rate of DPPH would therefore be due to reaction with free radicals formed during the autoxidation of mercaptans catalyzed by ferric ions.

## Discussion

The results described in the previous section define a kinetic scheme which involves rapid formation of a ferric-thiol complex, a slow rate-determining reduction of the complex by mercaptan, and finally rapid regeneration of the active iron(III) complex by autoxidation. The stoichiometry of the reaction (1 mole of oxygen oxidizing 4 moles of mercaptan) suggests that the oxygen is completely reduced to water. Thiyl radicals appear to be intermediates in the oxidative process.

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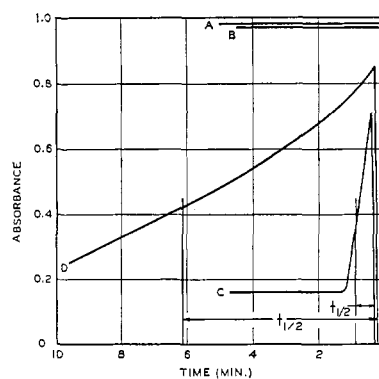
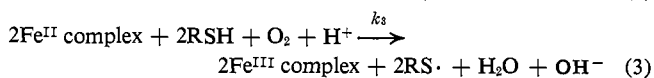
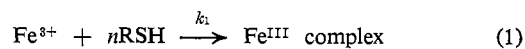


Figure 4. Reaction of diphenylpicrylhydrazyl (DPPH) with 2,6-heptanedithiol and 2,6-heptanedithiol-ferric complex in DMSO; absorbance of DPPH measured at 527  $m\mu$  vs. time. (A)  $[DPPH] = 9.31 \times 10^{-6}$  mole/l.;  $[Fe^{3+}] = 2.49 \times 10^{-5}$  mole/l. (B) Solution A after oxygen bubbled through for 5 min. (C) (solution of dithiol injected into solution B):  $[DPPH] = 9.05 \times 10^{-6}$  mole/l.;  $[Fe^{3+}] = 2.42 \times 10^{-5}$  mole/l.;  $[SH] = 27.90 \times 10^{-5}$  mole/l. (D) (in oxygen saturated solution):  $[DPPH] = 9.19 \times 10^{-6}$  mole/l.;  $[SH] = 28.30 \times 10^{-5}$  mole/l.

The following reaction scheme seems to be consistent with these results.



For mercaptan to iron ratios where reaction 1 is fast in comparison to the subsequent steps, the rate equation for mercaptan consumption can be written as

$$-\frac{d[SH]}{dt} = k_2[Fe^{III}][RSH] + k_3[Fe^{II}]^2[RSH]^2[O_2][H^+] \quad (5)$$

where  $Fe^{III}$  and  $Fe^{II}$  are the concentrations of the ferric- and ferrous-thiol complexes, respectively. Assuming a steady-state concentration for  $[Fe^{II}]$ , eq. 5 can be rewritten as eq. 6. The ferric complex con-

$$-\frac{d[SH]}{dt} = 2k_2[Fe^{III}][RSH] \quad (6)$$

centration can be considered a simple function of the ferric sulfate added,  $[Fe^{III}] = f[Fe^{3+}]$ , and the proportionality factor incorporated into the rate constant. The experiments were carried out at mercaptan concentrations where the reaction becomes pseudo-zero-order with respect to the mercaptan. Thus, the experimentally observed rate constants  $K$  of eq. 7 is com-

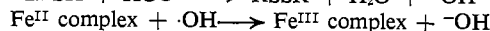
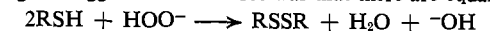
$$-\frac{d[SH]}{dt} = K[Fe^{3+}] \quad (7)$$

posed of

$$K = 2k_2f[RSH]_0 \quad (8)$$

$[RSH]_0$  signifies the concentration at which the change to pseudo-zero-order with respect to mercaptan occurs.<sup>22</sup>

(22) A good suggestion of a referee was that there are equally plausible reactions for the partially reduced oxygen species. Inclusion of these reactions in the kinetic scheme would change the over-all kinetic



ible reactions for the partially reduced oxygen species. Inclusion of these reactions in the kinetic scheme would change the over-all kinetic

The slopes of the curves in Figure 1 yielded the pseudo-first-order rate constants ( $K$ ) for the different dithiols. These constants are summarized in Table IV.

**Table IV.** Relative Oxidation Rates of Thiols in Dimethyl Sulfoxide

Compd.	$K$ , min. <sup>-1</sup>	Relative rate
2,6-Heptanedithiol	1.64	1
2,5-Hexanedithiol	3.55	2.2
2,4-Pentanedithiol	25.8	15.1
Poly(vinyl mercaptan) <sup>a</sup>	50.6	30.8

<sup>a</sup> SH = 0.10 mole/l.

The ease of oxidation increases as the distance between sulfhydryl groups decreases, thus confirming the results of Barron<sup>5</sup> and Overberger and Ferraro.<sup>13</sup> Although polyvinyl mercaptan oxidizes faster than 2,4-pentanedithiol, a polymer effect of the magnitude predicted from the oxidations by 2,6-dichlorophenolindophenol was not observed. Apparently the enhanced rate reported for the polymer was an artifact of a complex series of reactions occurring during the dye oxidation.

**Polymer Effects.** In addition to a slight rate enhancement over the dithiol model compound, polyvinyl mercaptan exhibited other characteristic differences. The formation and reduction of the polymercaptan-ferric complex occurred more slowly than the corresponding reactions of 2,4-pentanedithiol. This phenomenon could also be observed from the rate of oxygen consumption for low concentrations of polymer. One would expect these effects to be reversed because the local concentration of sulfhydryl groups on the polymer chain is much higher than the concentration of pentanedithiol in high dilution. These observations suggest that the actual concentration of

equation to

$$-\frac{d[\text{RSH}]}{dt} = 4k_2[\text{Fe}^{\text{III}}][\text{RSH}]$$

but would not affect the relative rates measured. We had not given much weight to the oxidation of mercaptan by hydrogen peroxide because this reaction is very slow in the absence of transition metal catalysts. Therefore, we favored reaction 5 for the decomposition of the intermediary hydroperoxide.

mercapto groups capable of being oxidized is less than the mercaptan titer of the polymer solution. The conformation of the polymer chain, especially when stabilized by a few disulfide linkages, could render sequences of sulfhydryl groups inaccessible. These sequences would be analogous to the "sluggish" sulfhydryl groups found in proteins. As a result of this reduction in freely reactive mercapto substituents, the ratio of effective mercaptan to iron(III) concentrations falls below the threshold value required for pseudo-zero-order dependence, and fractional order with respect to mercaptan is observed.

Another aspect of the polymer effect is the mobility of sulfhydryl groups attached to a polymer chain. The polymer does not precipitate during the initial 30% of reaction, indicating that intramolecular disulfide formation is the predominate mode of oxidation. The formation of cyclic disulfide units along the polymer backbone would reduce the flexibility of the polymer chain. Since the ferric ion is bound to the polymer in a thiol complex, the mobility of this active complex is governed by the polymer. To complete an oxidation-reduction cycle the complex must be brought in contact with a sulfhydryl group and the thiyl radicals formed must combine. Considering the reduced mobility of the polymer chain, other steps in the oxidation may be slowed to rates comparable to the rate-controlling ferric-thiol complex reduction step. These steps could contribute to the order of reaction and cause fractional mercaptan dependency.

Support for these hypotheses was gained by studying the influence of molecular weight on the oxidation rate of the polymer. The most significant effect observed was a decrease in the order of reaction with respect to mercaptan as the molecular weight decreased. For a series of polymers which had intrinsic viscosities of 0.45, 0.21, and 0.09 before hydrolysis, the order of reaction was found to be 0.32, 0.26, and 0.19, respectively. The higher molecular weight polymers would tend to be less mobile and also would be more effective in shielding the sulfhydryl groups.

Future publications will be concerned with the effect of stereochemistry of both polymeric and dithiol compounds on the oxidation. The influence of neighboring substituents other than sulfhydryl will also be reported.