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PRODUCTION OF THIYL RADICALS AND INVESTIGATION OF THEIR REACTIONS WITH OXYGEN AND 2-SULFOETHANETHIOSULFURIC ACID

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It has been supposed that thiyl radicals (RS•) are the main primary products from the transformation of thiols and disulfides during radiolysis and photolysis of their aqueous solutions [1, 2] and also some oxidation reactions of thiols [3]. Here the formation of RS• is accompanied by other processes. The radiolytic and photolytic generation of RS• can be modeled by chemical methods, which are more suitable for investigation of the characteristics of RS• radicals.

Intermediate products with higher degrees of oxidation of the thiols than RS•, formed evidently as a result of subsequent reaction of RS• with the oxidizing agent, have been observed during the action of various one-electron oxidizing agents of thiols [4]. Such subsequent reactions greatly hinder investigation of the chemical characteristics of RS• radicals. The oxidation of thiols by ferricyanide also cannot be considered a convenient method for the generation of RS• on account of the susceptibility of ferricyanide to form mixed-ligand complexes, which complicates the investigated system.

The use of the 1,10-phenanthroline complex $[Fe(phen)_3]^{3+}$ (I) as a one-electron oxidizing agent has a series of advantages, particularly when the investigations are carried out in the presence of O_2. The complex (I) does not add other ligands, and other intermediate products are not formed in its presence, in contrast to Fenton's reagent [5]. The product from the reduction of (I), i.e., the complex $[Fe(phen)_3]^{2+}$, can only exchange the phenanthroline ligands only for ligands complexing most strongly with Fe(II) and then fairly slowly. A further advantage of (I) is the absence of a restriction on the upper limit of the working pH value, which in work with Ce(IV), for example, must be <1.5 in order to prevent hydrolysis. At pH > 1 the complex (I) oxidizes water, but (as shown experimentally) the rate of this reaction is significantly lower than the rate of the reaction of (I) with thiols under almost any conditions. In order to reduce the reaction of (I) with water to a minimum it is necessary to keep the solution of (I) in an acidic medium and to realize the reaction at the required pH value by rapidly mixing the reagents in a flow.

The aim of the present work was to study the reaction of thiols with (I) and also the reactions of the RS• radicals which form. Aminothiols were selected as subjects for

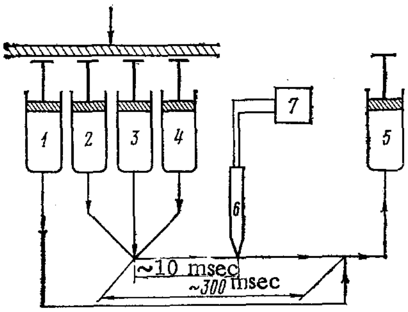

Fig. 1. Diagram of the apparatus for investigation of the reactions in the flow. Syringes containing solutions of hydrochloric acid (1), thiol (2), $[Fe(phen)_3]^{3+}$ (3), and 2-sulfoethanethiosulfuric acid (4), the receiving syringe (5), detector for measurement of $[O_2]$ in the solution (6), and measuring instrument (7).

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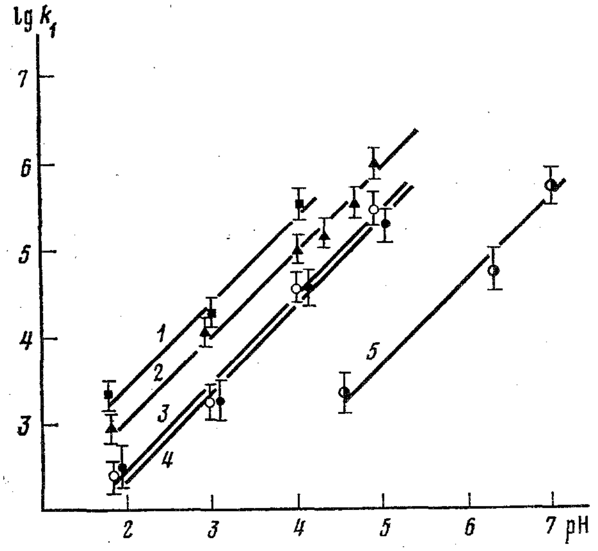

Fig. 2. Dependence of the rate constant k_1 of the second-order reaction between $[Fe(phen)_3]^{3+}$ and thiols on the pH of the solution (the pK_a values of the SH groups of the thiols are given in parentheses): 1) 2-(dimethylamino)ethanethiol (7.95, [9]); 2) 2-aminoethanethiol (8.35, [10]); 3) 3-aminopropanethiol (9.3); 4) 2-mercaptoethanol (9.6 [10]); 5) 4-aminobutanethiol (9.5).

investigation on account of their wide use in biology. Mercaptoethanol was also studied for comparison.

EXPERIMENTAL

The aminothiols were prepared by an improved version of the method in [6]. The concentration of the thiols in solution was determined by Ellman's method [7]. The products from oxidation of the aminothiols were separated on ion-exchange resin Dowex-50W × 12 (100-200 mesh) in the H^+ form. The activity of the ^{35}S-labeled compounds was determined in a ZhS-103 liquid scintillator on a Nuclear Chicago Mark-2 counter.

The complex $[Fe(phen)_3]^{2+}$ was obtained according to [8]. For preparation of (I) a $2 \cdot 10^{-1}$ M solution of $[Fe(phen)_3]^{2+}$ was added to a solution of 3 M sulfuric acid to a concentration of $1 \cdot 10^{-2}$–$4 \cdot 10^{-2}$ M, and lead dioxide was then added until the solution had acquired a blue color. The precipitate was separated by centrifuging, the filtrate was diluted twice with 8 M sulfuric acid, and the product was used within 5 h after preparation. Just before use the solution was diluted again with 100 times the amount of water. The concentration of (I) in the obtained weakly acidic solution decreases at a rate of 5% in 15 min, and the solution must therefore be used immediately after preparation.

TABLE 1. Rate Constants for the Oxidation of the Thiols (k_1) by the $[Fe(phen)_3]^{3+}$ Complex in Solutions with Various Ionic Strengths

Thiol	pH	k_1, liter/mole·sec	
		$\mu=0{,}3$	$\mu=0{,}9$
2-Aminoethanethiol	1,75	608±50	706±50
	3,95	$1{,}1\pm0{,}5\cdot10^5$	$0{,}93\pm0{,}05\cdot10^5$
2-Mercapto-ethanethiol	1,8	260±20	140±20
	2,9	1800±150	1000±100
	3,95	$3{,}1\pm0{,}2\cdot10^4$	$1{,}7\pm0{,}1\cdot10^4$

TABLE 2. Second-Order Rate Constants [k_2, reaction (2)] for Various Thiols at Ionic Strength $\mu = 0.3$

Thiol	$k_2 \cdot 10^{-9}$, liter/mole·sec
2-Aminoethanol	2,5±0,2
2-(Dimethylamino) ethanethiol	2,2±0,2
3-Aminopropanethiol	6,3±0,7
4-Aminobutanethiol	1,7±0,2
2-Mercaptoethanol	10±1

The 2-sulfoethanethiosulfuric acid (II) was obtained by the reaction of 2-bromo-1-ethanesulfonic acid with sodium thiosulfate.

In order to obtain solutions with various concentrations of oxygen the solutions were first freed from oxygen by bubbling argon and were then taken in a syringe in such a way that the gas phase did not remain. They were then mixed in the syringe with a measured quantity of water saturated with oxygen. The concentration of oxygen in the solutions was measured by polarography by means of an electrode coated with a polyethylene membrane.

The kinetics of the reaction of (I) with thiols were monitored by spectrophotometry from the increase in the concentration of $[Fe(phen)_3]^{2+}$. For this purpose we used a DV-2 spectrophotometer and an Aminco Stopflow attachment.

The measurements were made by a double-beam technique with wavelengths of 490 nm for the measurement beam and 770 nm for the reference beam. The signal from the spectrophotometer was recorded on the storage screen of an oscillograph. The other reactions were studied on the apparatus shown in Fig. 1. In order to measure the concentration of oxygen during the reaction in the flow we mixed the following solutions (Fig. 1): 1) acetate buffer + $4 \cdot 10^{-3}$ M 2-aminoethanethiol (syringe 2); 2) 0.057 M H_2SO_4 + $2 \cdot 10^{-4}$ M (I) (syringe 3) in ratios of 1:1. Syringes 1 and 4 here were disconnected. The pH values of the solutions after mixing amounted to 4.3. About 10 msec after mixing the solution was brought into contact with the polarographic electrode for measurement of $[O_2]$.

In order to study the final products from the reaction of (I) with the thiols in the presence of oxygen and (II) the following three solutions were mixed in the flow (Fig. 1): 1) a solution of the thiol in a buffer solution (syringe 2); 2) a solution of (I) in 0.057 M sulfuric acid (syringe 3); 3) a solution of (II) in water (syringe 4) in a ratio of 1:1:0.28.

Solutions 1 and 3 did not contain oxygen; solution 2 contained a specific amount of oxygen. After 0.3 sec after the solutions were mixed a solution of hydrochloric acid was introduced into the flow by means of syringe 1 so that the pH of the solution decreased to one. Such acidification of the solution after completion of the investigated reactions was necessary in order to reduce the contribution from the nucleophilic substitution reaction between the thiol and (II) to a minimum. The solution then passed into the syringe-receiver 5. Throughout the experiment the solution never came into contact with the gas phase. The concentration of oxygen and other compounds in the solution was then measured.

DISCUSSION OF RESULTS

Reactions of Thiols with (I). The kinetics of the reaction of the thiols with (I) were investigated under the following conditions: $[\text{thiol}] = 1 \cdot 10^{-2}-1 \cdot 10^{-4}$, $[(I)] = 1 \cdot 10^{-4}-1 \cdot 10^{-5}$ M, 20-22°C. The concentration of the thiol was always at least three times higher than the concentration of (I). Under these conditions at $pH > 1.5$ the reaction is of first order in each of the reagents and can be characterized formally by a second-order reaction rate constant (k_1). The values of k_1 for various thiols, depending on the pH, are given in Fig. 2. The values of the ionization constants of the mercapto groups $K_{\alpha}SH$, given in Fig. 2 for curve 1, were taken from [9], those for curves 2 and 4 were taken from [10], and those for curves 3 and 5 were determined by ourselves by spectrophotometry.

The dependence of k_1 on the pH of the solution and also on $K_{\alpha}SH$ makes it possible to suppose that only the thiol molecules in which the mercapto group is deprotonated take part in the reaction. It is therefore possible to propose the following reaction mechanism:

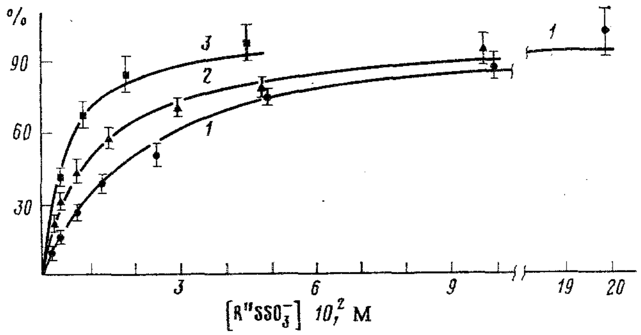

Fig. 3. Dependence of the loss of O_2 (1 and 2) and the formation of $H_3\overset{+}{N}CH_2CH_2SSO_3^-$ (I) + $^-O_3SCH_2CH_2SSCH_2CH_2\overset{+}{N}H_3$ (II) (3) on $[^-O_3SCH_2CH_2SSO_3^-]$. $[O_2] = 1.2 \cdot 10^{-4}$ (1 and 3) and $6.7 \cdot 10^{-5}$ M (2); $[Fe(phen)_3]^{3+} = 2.5 \cdot 10^{-5}$ (1 and 3) and $1.36 \cdot 10^{-5}$ M (2). The percentage ratio of $\Delta[O_2]$ for curves 1 and 2 and [(I)] + [(II)] for curve 3 to the total number of moles of RS· radicals formed in the reaction, divided by the volume of the solution, is plotted against the ordinate axis; $[RSH] = 10^{-3}$ M, pH 4.3.

$$RSH \rightleftarrows RS^- + H^+ \text{ (fast stage)} \tag{1}$$

$$RS^- + [Fe(phen)_3]^{3+} \rightarrow RS\cdot + [Fe(phen)_3]^{2+} \text{ (controlling stage)} \tag{2}$$

Comparison of the kinetic salt effect for 2-mercaptoethanol and 2-aminoethanethiol (III) (Table 1) confirms the idea that only the molecules of the thiol with a deprotonated mercapto group take part in the reaction. Since the amino group in (III) is protonated at the pH values indicated in Table 3, the total charge on the thiol molecule with the deprotonated mercapto group is equal to zero for (III) and to −1 for mercaptoethanol.

In accordance with the equation for reaction (2) the true rate constant for the second-order reaction between (I) and the thiols (k_2) must be calculated from the concentration of the thiol with the deprotonated mercapto groups $[RS^-]$, i.e., $k_2 = k_1 \cdot Q$, where Q is the ratio $[RSH]/[RS^-]$ in the solution for a given pH value and [RSH] is the total concentration of the thiol in the solution. In Table 2 the k_2 values are given for various thiols, calculated from the k_1 and K_a^{SH} values. Unlike k_1, k_2 does not depend on the pH of the solution and depends little on the nature of the thiol.

Transformations of the Thiyl Radicals in the Presence of Oxygen and 2-Sulfo-1-ethanethiosulfuric Acid. We studied the oxidation of the thiol by the complex (I) in greater detail for (III) with $[(I)] \approx 2 \cdot 10^{-5}$, $[(III)] \approx 1 \cdot 10^{-3}$–$1 \cdot 10^{-4}$, and $[O_2] \approx 1 \cdot 10^{-4}$ M. The measurements were made on the apparatus described above (Fig. 1). It was found that at pH > 1.5 the final product from the transformation of the thiol is the disulfide. Here 1 mole of the disulfide is formed for 2 g-ion of the complex (I), and the decrease in the amount of the thiol amounts to 2 mole. It was also found that $[O_2]$ had not changed in the solution after completion of the reactions. The overall reaction between (I) and (III) can be represented in the form of Eq. (3). In the absence of O_2 this reaction can be derived from reactions (1) and (2) and the recombination of thiyl radicals (4) $k_4 = 1 \cdot 10^{10}$ liter/mole·sec [11]:

$$2RSH + 2[Fe(phen)_3]^{3+} \rightarrow RSSR + 2[Fe(phen)_3]^{2+} + 2H^+ \tag{3}$$

$$RS\cdot + RS\cdot \rightarrow RSSR \tag{4}$$

In the presence of oxygen, however, reaction (5) competes with reaction (4). In the case of cysteine $k_{5\,for} = 8 \cdot 10^9$ liter/mole·sec [12]:

$$RS\cdot + O_2 \rightleftarrows RSOO\cdot \tag{5}$$

In [13, 14] various paths were proposed for the subsequent transformation of RSOO·. However, from the composition and ratio of the final products in the (III) + (I) + O_2 system it follows that of all the reactions of RSOO• proposed in [13, 14] only reactions (6) and (7) are possible under the conditions of our experiments. In order to make a choice between reactions (4), (6), and (7), leading to the same final products, we studied the effect of 2-sulfo-1-ethanethiosulfuric acid (II) in the reaction mixture:

$$RSOO\cdot + RSOO\cdot \rightarrow RSSR + 2O_2 \qquad (6)$$

$$RSOO\cdot + RS\cdot \rightarrow RSSR + O_2 \qquad (7)$$

It is known that RS• reacts rapidly with disulfides according to reaction (8), forming mixed disulfides [15]. If (II) is present in the solution, by analogy with reaction (8), reactions (9) and (10) can be expected to occur:

$$RS\cdot + R'SSR' \rightarrow RSSR' + R'S\cdot \qquad (8)$$

$$RS\cdot + R''SSO_3^- \rightarrow RSSO_3^-\,(I) + R''S\cdot \qquad (9)$$

$$RS\cdot + R''SSO_3^- \rightarrow RSSR''\,(II) + \cdot SO_3^- \qquad (10)$$

where $R = H_3\overset{+}{N}CH_2CH_2$ and $R'' = {}^-O_3SCH_2CH_2$.

The $SO_3^{\overline{\cdot}}$ radical formed in reaction (10) reacts with O_2 according to reaction (11).

$$SO_3^{\overline{\cdot}} + O_2 \rightarrow SO_5^{\overline{\cdot}}$$

$$2k_{11} \approx 1\cdot 10^9 \text{ liter/mole}\cdot\text{sec [16]}. \qquad (11)$$

Thus, if (II) is present in the solution, competition for RS• will be observed between O_2 and (II). Reaction (9) leads to substitution of RS• by R"S•, which must differ little from RS• with respect to the characteristics which we are considering, i.e., the system changes little as a result of reaction (9). In the final count reaction (5) does not lead to a requirement for O_2 from the solution on account of reactions (6) and (7) which follow it. Reaction (10) leads to a requirement for O_2 in reaction (11) which follows it. The competition between reactions (5) and (10) must lead to a somewhat unusual relationship. During the generation of RS• in the solution in the presence of (II) the requirement for O_2 from the solution will be lower, the higher the concentration of O_2 in the solution. The experimental data presented in Fig. 3 confirm this (curves 1 and 2).

Let us now consider reaction (9). In Fig. 3 curve 3 shows the sum of the concentrations of the products $RSSO_3^-$ and RSSR", formed in reactions (9) and (10). This sum was determined from the activity remaining in the solution after separation from the initial compound (III) on the cation-exchange resin and also from the disulfide formed in reactions (6) and (7). For such a determination we used (III) labeled with ^{35}S. Curves 1-3 were obtained by calculation of the competing reactions. Here, by trial and error we selected the values of the ratio k_5/k_{10} for curves 1 and 2 and $k_5/(k_9+k_{10})$ for curve 3 so that the obtained curve corresponded as closely as possible to the experimental points. The following results were obtained: $k_5/k_{10} = 170 \pm 30$ and $k_{10}/k_9 = 0.31 \pm 0.05$. From the values of the ratio k_{10}/k_9 it follows that the smallest part of all the RS• radicals generated in the solution was substituted by R"S• on the initial sections of curves 1 and 2, and the largest part was substituted on the final sections of the curves. The satisfactory agreement between the curves and the experimental points throughout indicate that RS• and R"S• differ little in their characteristics in the reactions considered above. From the fact that the experimental points on curves 1 and 2 go to saturation and that the requirement here for O_2 for each $SO_3^{\overline{\cdot}}$ radical formed approximates to 100% it follows that the $SO_5^{\overline{\cdot}}$ formed in reaction (11) does not lead subsequently to chain oxidation products under the given conditions.

We will now demonstrate that, of reactions (4), (6), and (7), reaction (6) makes the major contribution under the experimental conditions.

Reaction (4) cannot be the major reaction, since if it dominated, O_2 would not compete for RS•, and this contradicts the experimental data given in Fig. 3. Let us now consider the role of reaction (7). Under the experimental conditions the rate of the forward reaction (5) is much higher than the rate of reaction (7). This follows from the fact that k_7 cannot be much larger than k_5, since k_5 is close to the limit defined by diffusion, and $[O_2]$ is much greater than [RS•] under the conditions of the given experiments. Reaction (7) can therefore only dominate in the case where the equilibrium of reaction (5) is shifted strongly to the left, since only in this case will the concentration [RSOO•] and, consequently, the rate of reaction (7) be directly proportional to $[O_2]$ in the solution. Here the competition between reactions (7) and (10) can be described by the curves in Fig. 3. In this case, however, [RS•] will be much greater than [RSOO•], and reaction (4) will become determining, since it is not possible that $k_7 \gg k_4$. Reaction (7) can therefore also be excluded from the number of dominating reactions.

Measurement of O_2 in the solution after ≈10 msec after the regeneration of RS• showed that at this time $[O_2]$ had decreased by $\lesssim 1.3 \cdot 10^{-5}$ M with the total integral concentration of the RS• formed equal to $1 \cdot 10^{-4}$ M, which corresponds to the amount of reacted oxidizing agent. In this experiment $\tau_{1/2}$ for the regeneration of RS• was ∿1.5 msec. Therefore, during determination of k_6 we assume that approximately all $1 \cdot 10^{-4}$ M of the RSOO• radicals were formed instantaneously in reactions (2) and (5). From this we obtained the lower limit for the value of k_6: $2k_6 > 8 \cdot 10^6$ liter/mole•sec.

The (I) + (III) + O_2 System in a Strongly Acidic Medium. In a strongly acidic medium the reaction order in the investigated system depends on the concentration of (III). In order to study the reaction products the experiment was carried out under the following conditions: $[(I)] = 5 \cdot 10^{-5}$, $[(III)] = 1 \cdot 10^{-4}$, $[HCl] = 0.05$, $[H_2SO_4] = 0.06$, $[O_2] = 1.43 \cdot 10^{-4}$ M. In the experiment we used (III) labeled with ^{35}S. It was found that the decrease in the concentration of oxygen is given by $\Delta[O_2] = (1.55 \pm 0.15) \cdot 10^{-5}$ M. The ratio of the concentration of (I) taken for the reaction to the decrease in the concentration of (III) was equal to 1.5 ± 0.05. The concentration of taurine RSO_3H, equal to $(1.5 \pm 0.2) \cdot 10^{-5}$ M, was determined from the activity of the solution passed through the cation exchanger.

If it is supposed that the oxidation of the thiol under the indicated conditions is described by two equations (12) and (13):

$$RSH + 2[Fe(phen)_3]^{3+} + O_2 + H_2O \rightleftarrows RSO_3H + 2[Fe(phen)_3]^{2+} + 2H^+ \tag{12}$$

$$2RSH + 2[Fe(phen)_3]^{3+} \rightleftarrows RSSR + 2\,[Fe(phen)_3]^{2+} + 2H^+ \tag{13}$$

and the values taken from the experiment, $[(I)]/\Delta[(III)] = 1.5$ and $[(I)] = 5 \cdot 10^{-5}$ M, are used, the solution of the set of equations formulated on the basis of the last four equalities gives the concentration of the obtained taurine as $[RSO_3H] = 1.67 \cdot 10^{-5}$ M, which within the error limits coincides with the experimental values given above. The decrease of $[O_2]$ according to Eq. (12) must be equal to the gain in taurine, which within the experimental error limits also coincides with the experimentally obtained value of $\Delta[O_2]$. The agreement between the calculated and the experimental values indicates the absence of other products apart from those included in Eqs. (12) and (13) within the accuracy limits of the measurements. From this it can be concluded that with decrease in the pH value reactions (2) begin to accompany the other oxidation reactions, as a result of which O_2 added to RS• is no longer released back into the solution and, moreover, after the first stage of oxidation of the thiol [reaction (2)] a further quantity of (I) is brought into reaction. Here the thiol is converted finally into the sulfonic acid.

It remains unclear as to why the reaction mechanism changes in strongly acidic solutions. One of the possible reasons is reaction of the RSOO• which forms with the unreacted (I). The second possible reason is isomerization of RSOO• with cleavage of the O—O bond. The possibility of the last reaction was mentioned earlier in [1]. In addition, we established that $\mathrm{R}\overset{\mathrm{O}}{\overset{/\!\!/}{\mathrm{S}}}\!-\!\mathrm{O}\cdot$, obtained during the oxidation of $\mathrm{R}\overset{\mathrm{O}}{\overset{/\!\!/}{\mathrm{S}}}\!-\!\mathrm{OH}$ by the action of (I), adds oxygen irreversibly. Consequently, if this radical is formed in our system, it will be subject to further oxidation and can give taurine. In strongly acidic solutions, on account of the low rate of generation of RS•, the rate of reaction (6) will be low, and both above-mentioned reasons may therefore become significant, whereas at pH > 1.5 they are insignificant on account of the short lifetime of RSOO•, due to its disappearance in reaction (6).

It is clear that in this case the pH value of 1.5 should not be a strict boundary in the variation of the stoichiometry and mechanism of the reactions in the (I) + thiol + O_2 system and may change with variation in the experimental conditions and the nature of the thiol.

It is interesting to note that a requirement for O_2 from the solution and the formation of taurine are also observed during γ-radiolysis of (III), where the generation rate of RS• is comparable with the reaction rate of (I) and (III) at pH < 1.5. During the γ-radiolysis of thiols, however, the requirement for O_2 from the solution occurs in a very wide range of pH. In this the pattern of the radiolysis of thiols in the presence of oxygen differs substantially from oxidation in the (I) + thiol + O_2 system.

CONCLUSIONS

1. The kinetics of the oxidation of 2-aminoethanethiol, 3-aminopropanethiol, 4-aminobutanethiol, (dimethylamino)ethanethiol, and 2-mercaptoethanol by the 1,10-phenanthroline complex $[Fe(phen)_3]^{3+}$ were studied. The complex $[Fe(phen)_3]^{3+}$ only reacts with thiols containing a deprotonated mercapto group.

2. The stoichiometry and the reaction products in the 2-aminoethanethiol + $[Fe(phen)_3]^{3+}$ + oxygen system were studied.

3. 2-Sulfo-1-ethanethiosulfuric acid can be used as reagent for thiyl radicals.

4. The differences between the processes occurring in the thiol + $[Fe(phen)_3]^{3+}$ + O_2 system at $pH > 1.5$ and the reactions in which RS· radicals participate during radiolysis of the thiols in the presence of oxygen were determined.

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