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Oxidation of aminothiols by molecular oxygen catalyzed by copper ions. Stoichiometry of the reaction

G. A. Bagiyan,* I. K. Koroleva, N. V. Soroka, and A. V. Ufimtsev

B. P. Konstantinov Petersburg Institute of Nuclear Physics, Russian Academy of Sciences,
1 Orlova Roshcha, 188300 Gatchina, Leningrad Region, Russian Federation.
Fax: +7 (812) 713 8541. E-mail: heinrich@omrb.pnpi.spb.ru

Catalysis of oxidation of aminothiols by copper ions was studied depending on the structure of aminothiols and pH of the medium. The catalytic reaction proceeds in the inner coordination sphere of Cu^+. At pH 7—9, oxidation of bidentate aminothiols involves reduction of O_2 to H_2O_2. At pH 9—13, oxidation of chelating aminothiols is accompanied by reduction of O_2 to H_2O, whereas oxidation of weak-chelating aminothiols still proceeds by the former mechanism. In this process, the thiolate anions coordinated to the Cu^+ ions lose one electron each and are oxidized to amino disulfides, which go from the inner sphere of the Cu^+ complex into a solution. Procedures developed for the determination of amino disulfides, the chemiluminescence determination of H_2O_2 in the presence of aminothiols as luminescence quenchers, and a modified polarographic procedure for the determination of O_2 allowed us to establish that oxidation of aminothiols is not accompanied by catalytic decomposition of H_2O_2 that formed.

Key words: aminothiols, oxidation, amino disulfides, molecular oxygen, hydrogen peroxide, water, catalysis, copper ions, stoichiometry.

Recently, we have found[1] that self-oxidation of thiol compounds (TC) in aqueous solutions occurs due to contamination of solutions by impurities of variable-valence metal ions, which are generally present in industrially prepared TC. It was demonstrated that catalytic oxidation of thiols proceeds most efficiently in the presence of copper ions in aqueous solutions. For chelating aminothiols (AT), for example, for cysteine, the kinetic orders of the reaction depend strongly on pH, which reflects the probable change in the reaction mechanism. In contrast, for weak-chelating homocysteine, which is, apparently, oxidized according to the same mechanism throughout the pH range used, the reaction orders with respect to oxygen and copper remain virtually unchanged. These differences in the kinetic behavior of the above-mentioned structurally very similar TC (the hydrocarbon core of homocysteine contains only one CH_2 group more than cysteine) are, apparently, associated with the characteristic features of their complex formation with Cu^+ ions, which finally leads to substantial differences in interactions of catalytically active species with the O_2 molecule.

Under the conditions of catalytic oxidation, there is a complex equilibrium between different forms of copper complexes with aminothiols whose position depends both on the structure of AT and pH.[2]

$$Cu^+ + RS^- \rightleftharpoons 1/n\,[(Cu^+)(RS^-)]_n \tag{1}$$

$$2/n\,[CuSR]_n + RS^- \rightleftharpoons 1/n\,[(Cu^+)_2(RS^-)_3]_n \tag{2}$$

$$1/n\,[(Cu^+)_2(RS^-)_3]_n + RS^- \rightleftharpoons 2\,[(Cu^+)(RS^-)_2] \tag{3}$$

$$[(Cu^+)(RS^-)_2] + RS^- \rightleftharpoons [(Cu^+)(RS^-)_3] \tag{4}$$

In an alkaline medium, complexes with such ligands as cysteamine (ESH) generally form chelate structures, whereas the formation of such structures is hindered or does not take place at all in the case of complexes with weak-chelating (homocysteamine, PSH) or nonchelating ligands ($Me_3N^+CH_2CH_2SH$, TSH).*

These forms show different efficiency in the activation of the O_2 molecule by transforming it from the ground (triplet) to excited (singlet) state, in which oxygen serves as an electron acceptor. If the role of Cu^+ complexes with aminothiols is limited to this activation, the subsequent transformations outside the coordination sphere of the metal atom should lead to fixation of oxygen in the final reaction products (outer-sphere mechanism of catalysis). Actually, ESH was transformed into taurine (ESO_3H) upon radiolysis of aerated aqueous solutions of ESH at pH 7—8 or upon storage of its solution in 0.1 *M* HCl (up to 25% of the starting concentration of $1 \cdot 10^{-4}$ mol L^{-1}) in air for 4—5 weeks.[3,4] If catalytic oxidation was completed in the coordination sphere of a copper complex with aminothiol, inner-sphere oxidation of aminothiol would afford amino disulfides (AD), and O_2 would be

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* In the present study, all compounds containing the quaternary N atom were used as perchlorates.

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reduced to H_2O_2 (H_2O). Calculations have demonstrated[5] that the free-radical chain process could not be an alternative to the inner-sphere mechanism, because it would require that the rate constant of oxidation (W_0) be four orders of magnitude higher than that of the latter mechanism and that the concentration of hydroperoxide anions be stationary. The available methods of analysis are insufficiently sensitive for the determination of possible intermediates and final products of catalytic oxidation. In some cases, a known procedure for the determination of H_2O_2 [6] allows one to detect its presence in the AT + Cu^+ + O_2 reacting system only at a qualitative level. The situation is complicated by the fact that H_2O_2 reacts with aminothiols with a rather high rate[7,8] and the contribution of this reaction should be taken into account in studies of catalytic oxidation along with possible catalysis of decomposition of H_2O_2 by copper complexes with aminothiols. In the present study, we developed new procedures and used them in investigation of the formation of intermediates and final products of catalytic oxidation of aminothiols in the presence of Cu^+ ions in solution.

Experimental

The study was carried out with the use of aminothiols and products of their oxidation: $Me_3N^+CH_2CH_2SH$ (TSH), $[Me_3N^+CH_2CH_2S]_2$ (TSST), $Me_2NCH_2CH_2SH$ (DSH), $[Me_2NCH_2CH_2S]_2$ (DSSD), $H_2NCH_2CH_2CH_2SH$ (PSH), $[H_2NCH_2CH_2CH_2S]_2$ (PSSP), $H_2NCH_2CH_2SH$ (ESH), $[H_2NCH_2CH_2S]_2$ (ESSE), $H_2NCH_2CH_2SO_2H$ (ESO_2H), $H_2NCH_2CH_2SO_3H$ (ESO_3H), and $H_2NCH_2CH_2SSO_2CH_2CH_2NH_2$.

Aminothiols, including those labeled with the ^{35}S isotope, were synthesized and purified from possible impurities according to a known procedure.[9] Catalytic oxidation was carried out in solutions of a borate-phosphate buffer (BPB, $(1—3) \cdot 10^{-1}$ mol L^{-1}) prepared with the use of compounds of special purity. In kinetic experiments, the concentrations of aminothiols and copper compounds were varied in ranges of $1 \cdot 10^{-4}—1 \cdot 10^{-1}$ and $1 \cdot 10^{-7}—8 \cdot 10^{-5}$ mol L^{-1}, respectively. Oxidation products of aminothiols were analyzed[1] using paper chromatography.

The appearance of ^{35}S-labeled amino disulfides in solutions and the increase in their concentration in the course of catalytic oxidation and oxidation of aminothiols by hydrogen peroxide were monitored by binding residual aminothiol with complex mercury sulfide according to a procedure developed by us earlier.[10] This procedure made it possible to detect amino disulfides at concentrations of about $5 \cdot 10^{-6}$ mol L^{-1} with an accuracy of 5%, while the concentrations of aminothiols in solutions could be higher by a factor of 1000.

The concentrations of H_2O_2 in solutions in the course of catalytic oxidation were analyzed by a chemiluminescence procedure,[11] which allows one to determine H_2O_2 at concentrations of $5 \cdot 10^{-6}$ mol L^{-1} with an accuracy of ≤5% in the presence of up to $1 \cdot 10^{-2}$ mol L^{-1} of aminothiols serving as strong luminescence quenchers.

A decrease in the O_2 content in the course of catalytic oxidation was monitored using a modified polarographic method for analysis of O_2 on a Pt cathode, because the standard version of this method appeared to be unsuitable for solutions containing aminothiols, which appeared to be chemically aggressive resulting in rapid cathode poisoning. The method developed by us makes it possible to record the kinetics of a decrease in $[O_2]$ in an automatic mode, the error of the determination of $[O_2]$ in solutions was no higher than 5% at concentrations of $(2—100) \cdot 10^{-5}$ mol L^{-1}.

Results and Discussion

Analytical methods commonly used for studying catalytic oxidation of aminothiols in the presence of variable-valence metals do not allow one to vary the concentrations of reagents over wide ranges in kinetic experiments for several reasons. First, if the reaction rate is monitored by a decrease in [AT] or an increase in [AD] in solution, adequate results can be obtained only by measuring their concentrations in the range of $(1—5) \cdot 10^{-4}$ mol L^{-1} due to low solubility of O_2 in aqueous solutions. Second, the contribution of the reaction of aminothiol with H_2O_2 (possible intermediate in catalytic oxidation) to the AT and AD concentrations should be taken into account, which introduces an additional error into the results. Therefore, a procedure for studying the kinetics of catalytic oxidation of TC should be based on the observation of a decreasing concentration of O_2 in the AT + Cu^+ + O_2 reacting system. However, measurements of a decrease in $[O_2]$ with time by volumetric methods[12,13] requires sampling, which does not allow one to accurately detect rapid (in a matter of minutes) consumption of O_2 in solutions and gives no ways of overcoming rigid limitations on the concentrations of the participants of catalytic oxidation thus hindering the establishment of its mechanisms.

We modified the polarographic procedure for the determination of $[O_2]$ taking into account the characteristic features of the system under consideration, which enabled us to eliminate the above-mentioned drawbacks. We used a standard Clark-type oxygen electrode[14] in which the solution under study is separated from a polarographic cell by an O_2-permeable membrane, which prevents poisoning by solutions of aminothiols. However, such an electrode is characterized by a sluggish response (40—60 s), which does not allow one to study fast processes involving O_2. We succeeded in reducing the time of attainment of the stationary state on a cathode to 2—3 s as a result of a modification of a membrane electrode by making a slot (~2 μm) between the cathode and membrane and using Teflon films (10—15 μm) as the membrane, which enabled us to record a complete decrease in $[O_2]$ in solutions within a few minutes with an accuracy of ≤5%. A polarographic cell involves a measuring Pt electrode and reference silver-chloride electrode with a po-

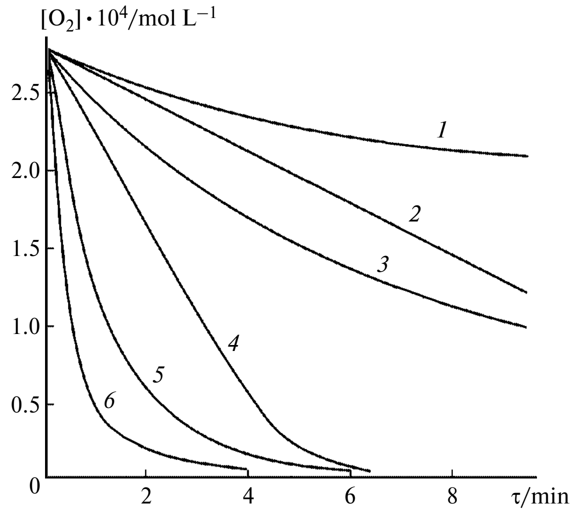

Fig. 1. Kinetics of a decrease in the concentration of O$_2$ in catalytic oxidation of 2-aminoethane-*N*-(3-aminopropyl)thiol (5 • 10^{-3} mol L^{-1}) in the presence of Cu$^+$ ions (8 • 10^{-5} g-ion L^{-1}) depending on pH of the medium: 6.0 (*1*), 11.5 (*2*), 7.0 (*3*), 10.0 (*4*), 8.0 (*5*), and 8.5 (*6*).

tential difference of 0.6 V. To prevent inleakage of atmospheric oxygen, the polarographic cell was placed using ground-glass joints in 3—10-mL closed temperature-controlled cells, which contained the solution under investigation stirred with a magnetic stirrer at a constant rotation speed. A decrease in [O$_2$] in the kinetic experiments was automatically recorded taking into account a change in the cathode current by sending a signal from the polarographic cell to an EPP-09 self-recorder, in contrast to volumetric methods for measuring [O$_2$] based on individual points.

Actually, an automatic recording of the kinetics of a decrease in [O$_2$] in catalytic oxidation (Fig. 1) makes it possible to vary the concentrations of aminothiol, copper, and O$_2$ over wide ranges (1 • 10^{-4}—1 • 10^{-1}, 1 • 10^{-7}—8 • 10^{-5}, and 2 • 10^{-5}—1 • 10^{-3} mol L^{-1}, respectively).

The degree of oxidation of aminothiols in catalytic oxidation was determined by analyzing different AT + Cu$^+$ + O$_2$ systems for various products with the use of paper chromatography, and their yields were evaluated depending on the acidity of the medium under conditions of both partial and complete conversion of aminothiols into catalytic oxidation products. In these experiments, ^{35}S-labeled aminothiols with different structures were oxidized by atmospheric oxygen in solutions with pH 5—11 in wide concentration ranges of AT and Cu. Then the reaction mixtures were separated on a paper in acidic chromatographic solvent systems to decelerate catalytic oxidation in the course of chromatographic separation with the use of specially synthesized ^{35}S-labeled aminothiol derivatives, which contained the sulfur atom in different oxidation states as references.[1] The experiments demonstrated that catalytic oxidation in AT + Cu$^+$ + O$_2$ systems afforded only one final product (within the radiochemical purity of the AT samples used (≥98%)), which was identical in the chromatographic mobility to the corresponding AD. Oxidation of aminothiols was not accompanied by the formation of their oxygen-containing derivatives, which made it possible to analyze the characteristic features of catalytic oxidation using a fast method developed by us for the determination of amino disulfides in the presence of a 1000-fold excess of aminothiols using complex mercury sulfide.[10] Actually, if catalytic oxidation afforded amino disulfide along, for example, with RSO$_3$H, the former compound would be incorrectly determined by this method because complex mercury sulfide precipitates neither amino disulfide nor RSO$_3$H.

Hence, catalytic oxidation in AT + Cu$^+$ + O$_2$ systems leads to the transformation of aminothiols only into amino disulfides.

The formation of oxygen-containing products was observed only in the reaction of H$_2$S with O$_2$ in the presence of copper complexes with dithio compounds, *viz*., unithiol and dithiosuccinic acid, in neutral and alkaline solutions. Actually, vigorous bubbling of air through carbonate solutions (pH 9) of hydrosulfide ions in concentrations of up to 1 mol L^{-1} containing unithiol (2 • 10^{-3} mol L^{-1}) and Cu$^+$ (4 • 10^{-4} g-ion L^{-1}) as the catalyst afforded a mixture of the sulfate and thiosulfate anions in 80—90% yield and elemental sulfur in only 10—20% yield. Apparently, the predominant formation of sulfate and thiosulfate anions[15] is attributable to the noncatalytic reactions of polysulfide ions, which are primary products of the catalytic reaction eliminated from the coordination sphere of the copper ion into the bulk of the solution, with O$_2$ according to radical-chain mechanisms.[1] The formation of these products can be prevented by binding polysulfide ions to form the R(S)$_n$R species resistant to O$_2$ through the thiol-disulfide interactions in the presence of high concentrations of RSSR in the AT + Cu$^+$ + O$_2$ reacting system.

Actually, the addition of AD, in particular, of cystamine (ESSE), in concentrations comparable with that of hydrosulfide ions (0.5—1.0 mol L^{-1}) to carbonate solutions of hydrosulfide ions, which were subjected to catalytic oxidation, sharply suppressed the formation of oxygen-containing sulfur compounds and their concentration became much lower than 1% due, apparently, to successive thiol-disulfide interactions

$$\mathrm{ESSS^- + ESSE \rightleftharpoons ESSSSE + ES^-}, \textit{etc.} \qquad (5)$$

These interactions gave finally the E(S)$_8$E and E(S)$_{10}$E species, which readily generated thermodynamically stable six- and eight-membered sulfur rings. The degree of formation of oxygen-containing sulfur compounds is of importance for estimating the applicability of a particular scheme in the technology of purification of natural gas from hydrogen sulfide, because the lower the percentage of the formation of oxygen-containing sulfur compounds the longer the absorbability of a carbonate solution is retained in the step of H_2S absorption.

The second reagent, *viz.*, molecular oxygen, in catalytic steps of oxidation can be reduced to $HO_2^{\bullet}$ ($O_2^{\bullet -}$), H_2O_2, or H_2O according to the corresponding one-, two-, or four-electron mechanisms of the interaction of O_2 with aminothiols in the coordination sphere of the Cu^+ ions. According to the single-electron scheme of reduction of O_2, the superoxide radicals should be eliminated from the coordination sphere of Cu^+ into the bulk of the solution, where these radicals either undergo rapid dismutation

$$HO_2^{\bullet} + O_2^{\bullet -} (+ H^+) \longrightarrow O_2 + H_2O_2, \qquad (6)$$

$$O_2^{\bullet -} + RSH (+ H^+) \longrightarrow RS^{\bullet} + H_2O_2, \qquad (7)$$

or are involved in radical-chain processes through the formation of the $RS^{\bullet}$ radicals to give finally oxygen-containing products of oxidation of aminothiols.[1] The absence of the latter among catalytic oxidation products indicates that these single-electron schemes are highly improbable.

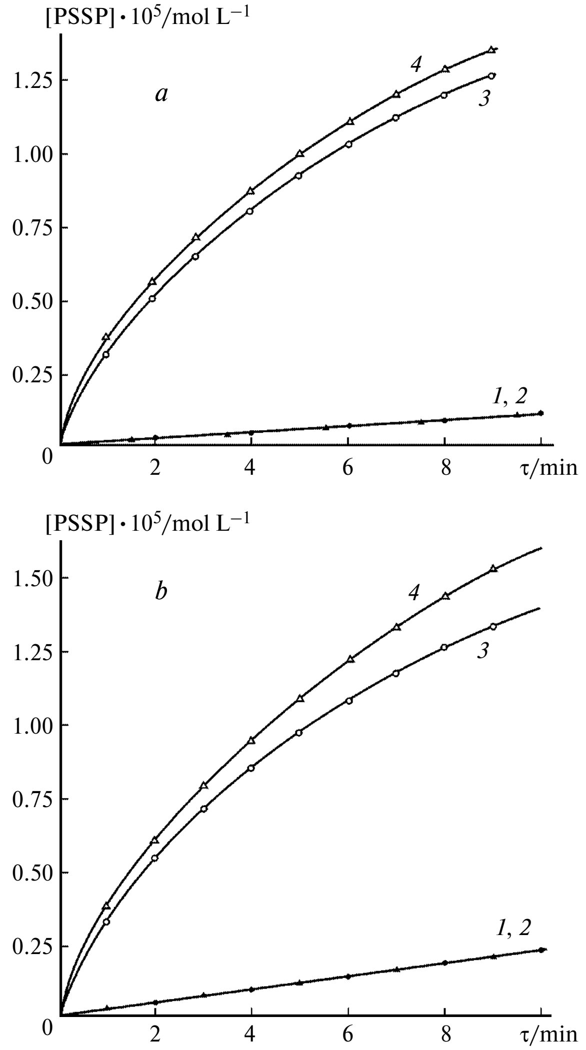

Fig. 2. Estimation of the contribution of the reaction of H_2O_2 with PSH at pH 8.0 (*a*) and 13.0 (*b*) in the PSH + H_2O_2 (*1*), PSH + H_2O_2 + Cu^+ (*2*), PSH + O_2 + Cu^+ (*3*), and PSH + O_2 + Cu^+ + H_2O_2 (*4*) systems based on accumulation of PSSP in solutions ($[PSH]_0 = 5 \cdot 10^{-4}$ mol L^{-1}, $[Cu^+] = 1 \cdot 10^{-7}$ g-ion L^{-1}, $[O_2]_0 = 3 \cdot 10^{-4}$ mol L^{-1}; $[H_2O_2] = 2.5 \cdot 10^{-4}$ mol L^{-1} (*1*, *2*, *4*)).

Before finding experimental conditions for the determination of the degree of reduction of O_2 (to H_2O_2 or H_2O) in catalytic oxidation of bidentate aminothiols containing one NH_2 group and one SH group, it was necessary to take into account and experimentally examine the following several factors: first, the degree of the involvement of H_2O_2 in pH-dependent noncatalytic oxidation of aminothiols;[7,8] second, the possibility of catalytic decomposition of H_2O_2 under anaerobic conditions in the presence of Cu^+ complexes with aminothiols; and third, the possibility of more complex catalytic decomposition of H_2O_2 in the presence of oxygen-containing Cu^+ complexes with aminothiols. The contributions of these reactions were estimated in special experiments in which an increase in the AD concentration with time under the conditions of catalytic oxidation of aminothiols was determined according to a known procedure[10] (Figs. 2 and 3). The experiments demonstrated that the noncatalytic reaction of H_2O_2 with aminothiols under the conditions used could result in the additional formation of amino disulfide in a yield from 3 (pH 8) to 15% (pH 13) of the total amount of the products in solutions. Both under aerobic and anaerobic conditions, H_2O_2 does not undergo catalytic decomposition under the action of Cu^+ complexes with aminothiols. This is evidenced by the fact that the addition of hydrogen peroxide to solutions of Cu^+ + AT or Cu^+ + AT + O_2 in amounts comparable with the AT concentration did not lead to a noticeable increase in the AD concentration in the solution, in contrast to traditional Haber—Weiss's systems[16] in which H_2O_2 molecules are decomposed into OH radicals. The possibility of such processes occurring in Cu^+ + AT systems could not be excluded based on the kinetic behavior of aminothiols with different structures in the course of catalytic oxidation in an alkaline medium, where the reaction orders with respect to Cu^+ increase to 2 for chelating aminothiols (for example, ESH), whereas the reaction orders for weak-chelating aminothiols (PSH) remain unchanged on going from neutral to alkaline solutions. However, our experiments demonstrated (see Figs. 2 and 3) that Cu^+ + AT systems did not act as catalysts for decomposition of H_2O_2 regardless of the structure of AT and kinetic orders of catalytic oxidation. This fact led to the conclusion that the catalytic reaction was com-

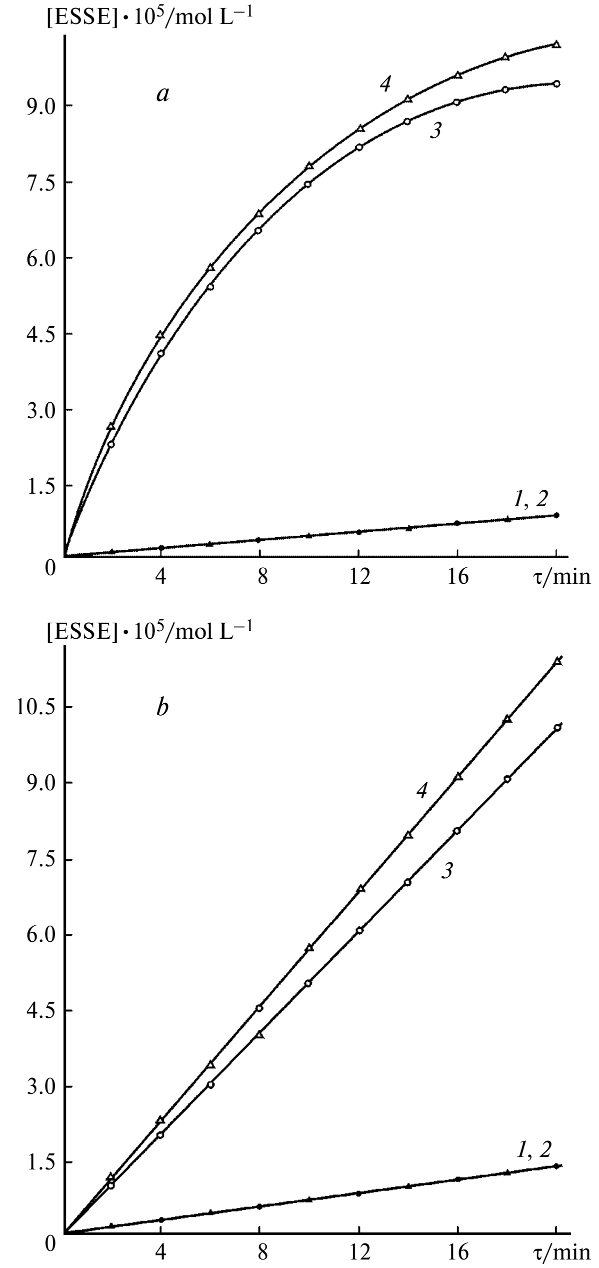

Fig. 3. Estimation of the contribution of the reaction of H_2O_2 with ESH in the ESH + H_2O_2 (*1*), ESH + H_2O_2 + Cu^+ (*2*), ESH + O_2 + Cu^+ (*3*), and ESH + O_2 + Cu^+ + H_2O_2 (*4*) systems at pH 7.0 (*a*) and 13.0 (*b*) based on accumulation of ESSE in solutions ($[ESH]_0 = 5 \cdot 10^{-4}$ mol L^{-1}, $[Cu^+] = 5 \cdot 10^{-7}$ g-ion L^{-1}, $[O_2]_0 = 3 \cdot 10^{-4}$ mol L^{-1}; $[H_2O_2] = 2.5 \cdot 10^{-4}$ mol L^{-1} (*1, 2, 4*)).

pletely proceeded in the coordination sphere of Cu^+ ion. Hence, it is only necessary to determine the state to which the O_2 molecule is reduced in the course of oxidation of structurally different bidentate aminothiols.

With the aim of substantially reducing the contributions of all the above-considered side reactions, we chose the following reaction conditions. In borate-phosphate buffers in the pH ranges of 6—8.5 and 11—13, aminothiols with different structures (10^{-3}—10^{-2} mol L^{-1}) were oxidized by O_2 ($5 \cdot 10^{-5}$—$3 \cdot 10^{-4}$ mol L^{-1}) in the presence of Cu^+ ($2 \cdot 10^{-6}$—$8 \cdot 10^{-5}$ mol L^{-1}). The reactions were carried out with stirring in a 3-mL reaction vessel equipped with a polarographic cell for measurements of $[O_2]$ with prevention of inleakage of atmospheric oxygen. After the addition of copper during one minute at different intervals, catalytic oxidation was retarded by acidification of the solutions with a small amount of HCl, then the residual concentration of O_2 was measured, and samples were withdrawn to determine [AD] using complex mercury sulfide and to evaluate $[H_2O_2]$ by a chemiluminescence method.[11] The degree of reduction of O_2 in catalytic steps of the catalytic oxidation process was determined from the ratio $\Delta[AT]/\Delta[O_2]$ and by comparing it with the measured $[H_2O_2]$ concentration in the reaction solution. The experiments demonstrated (Table 1) that the $\Delta[AT]/\Delta[O_2]$ ratio in the course of catalytic oxidation of nonchelating aminothiols remained constant (close to 2) throughout the pH range, and $[H_2O_2]$ generated as a result of catalytic oxidation was equal to $\Delta[O_2]$. The same ratios were obtained in the analysis of catalytic oxidation products for chelating aminothiols in the pH range of 6—8. These results indicate that catalytic oxidation of nonchelating aminothiols is accompanied by reduction of O_2 to H_2O_2 in the coordination sphere of Cu^+, like in the case of chelating aminothiols in neutral media. However, the $\Delta[AT]/\Delta[O_2]$ ratio for chelating aminothiols in alkaline media (pH 11—12) is close to 4 and the amount of H_2O_2 formed in solutions is $(0.3—0.1) \cdot \Delta[O_2]$. It should be noted that higher $[AT]/[Cu^+]$ ratios in solutions led to lower concentrations of H_2O_2 generated. Thus, $[H_2O_2] = 0.3\Delta[O_2]$ and $[H_2O_2] = 0.1\Delta[O_2]$ at $[AT]/[Cu^+] = 100$ and $[AT]/[Cu^+] = 1000$, respectively. Presumably, the latter ratios indicate that the catalytic steps of oxidation of chelating aminothiols in an alkaline medium involve predominantly four-electron reduction of coordinated O_2 because, according to the above-mentioned data, catalytic decomposition of H_2O_2 that formed can be excluded in the case of the outer-sphere reaction with Cu^+ complexes with aminothiols. In addition, it should be noted that the kinetics of a decrease in the concentration of aminothiol in the course of catalytic oxidation is not inhibited by HCOOK ($C \le 10^{-1}$ mol L^{-1}) serving as an acceptor of OH radicals,[3] which should be primary products upon catalytic decomposition of H_2O_2 by variable-valence metal complexes.

Therefore, the investigation of the stoichiometry of catalytic steps of the catalytic oxidation process showed that the reactions of bidentate aminothiols with O_2 occur, most likely, in the inner coordination sphere of Cu^+, are accompanied by oxidation of aminothiols to amino disul-

Table 1. Stoichiometry of reduction of O_2 on catalytic oxidation of aminothiols (AT) in the presence of Cu^+ ions

AT	$[AT] \cdot 10^3$	$[Cu^+] \cdot 10^6$	pH	τ/s	$-\Delta[O_2] \cdot 10^5$	$\Delta[AD] \cdot 10^5$	$\Delta[H_2O_2] \cdot 10^5$	$-\Delta[H_2O_2]^* \cdot 10^5$	$\Delta[AT]/\Delta[O_2]^{**}$
	mol L^{-1}				mol L^{-1}				
ESH	3	25.0	8.0	15	3.5	4.0	3.1	0.45	2.0
ESH	3	2.5	8.0	30	1.8	2.3	1.3	0.36	2.1
ESH	5	50.0	11.0	10	12.0	22.0	3.5	1.2	3.5
ESH	5	5.0	11.0	40	1.2	2.5	0.2	0.2	3.8
PSH	5	80.0	8.5	15	6.0	6.5	5.4	0.52	2.0
PSH	5	5.0	12.0	10	15.0	15.0	15.0	—	2.0

* A decrease in the concentration of H_2O_2 in the course of the noncatalytic reaction with aminothiol.

** $\Delta[AT]/\Delta[O_2] = 2\Delta[AD]/\Delta[O_2] = 2(\Delta[AD] - \Delta[H_2O_2])/\Delta[O_2]$.

fides and reduction of O_2 to H_2O_2 and/or H_2O, and can be formally described by the following equations

$$2\,RSH + O_2 \longrightarrow RSSR + H_2O_2, \qquad (8)$$

$$4\,RSH + O_2 \longrightarrow 2\,RSSR + 2\,H_2O. \qquad (9)$$

Equation (8) corresponds to oxidation of nonchelating aminothiols. Equations (8) and (9) correspond to oxidation of chelating aminothiols, the statistical weight of Eq. (9) being increased when catalytic oxidation is carried out in an alkaline medium and the $[AT]/[Cu^I]$ ratio in the solution is increased. It should be noted that the $[(Cu^+)(RS^-)_2]$ complexes prevail in the equilibria in the reactions of all aminothiols at pH 10—12. The data on catalytic oxidation obtained in the present study showed that O_2 coordinated in the complexes with chelating aminothiols is retained in the coordination sphere of Cu^+ until it is reduced to H_2O. The Cu^+ complexes with nonchelating aminothiols have, apparently, structures such that O_2, which is initially coordinated in these complexes, is eliminated from the coordination sphere of Cu^+ once being reduced to H_2O_2.

It should be emphasized that the characteristic features of the stoichiometry of catalytic oxidation were established for bidentate aminothiols whose alkaline solutions with copper ions contain the $[(Cu^+)(RS^-)_2]$ complexes as the major component with the ratio $[AT]/[Cu^+] \geq 100$. In the presence of Cu^+ complexes with tri- or polydentate ligands (for example, with $H_2N(CH_2)_3NH(CH_2)_2S^-$, $H_2N(CH_2)_2NH(CH_2)_2S^-$, or glutathione), solutions contain predominantly the polynuclear $[(Cu^+)(RS^-)]_n$ and $[(Cu^+)_2(RS^-)_3]_m$ complexes (see Eqs. (1) and (2)), which are inactive in catalytic oxidation of aminothiols by molecular oxygen but are very active in catalytic decomposition of H_2O_2.[17] Actually, the addition of equivalent amounts of H_2O_2 to aerated solutions of the first two aminothiols followed by the addition of copper ions led to vigorous decomposition of H_2O_2 and the corresponding oxidation of aminothiols.

The experimental data on the kinetics of catalytic oxidation of aminothiol by molecular oxygen in support of the inner-sphere mechanism will be published elsewhere.

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