INVESTIGATION OF RADIATION INDUCED OXIDATION OF THIOL COMPOUNDS IN AQUEOUS SOLUTIONS

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The SH-group is of functional importance in the active centers of a large number of ferments. On the other hand it is known that this is the most sensitive group in reference to radiation induced oxidation. Ionising radiation involves oxygen in the SH-groups oxidation reaction. The radiation yields of the oxidation of mercaptocompounds (RSH) are higher that the yield of water radicals even in the dilute solutions (10^{-3} M). Different mechanisms of reaction were assumed in a number of works [1 — 5], however, in [1] the authors point out that in terms of the assumed mechanisms, the important features of the experimental material cannot be explained. That is why a more detailed investigation of radiation induced oxidation of SH-compounds is desired.

In our work the objects of investigation were 2-aminoethanethiol (1) and 2-mercapto-1-sulfonic acid (II). In fig. are given the yields of loss oxygen at radiolysis (^{60}Co source; dose rate 630 rad/min) of aerated aqueous solutions of (1) (curves 1, 2, 3) and (II) (curves 4, 5, 6).

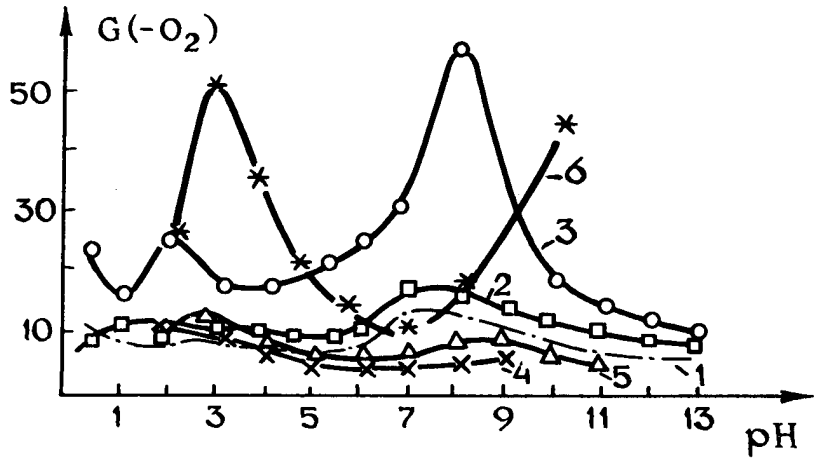

Fig. *1* — [RSH] = 10^{-3} M; *2* — [RSH] = $3 \cdot 10^{-3}$ M; *3* — [RSH] = $5 \cdot 10^{-2}$ M; *4* — [RSH] = 10^{-3} M; *5* — [RSH] = 10^{-2} M; *6* — [RSH] = 10^{-1} M

The excess of $G(-O_2)$ values over the value of water radicals ($G \approx 6$) cannot be explained by the chain reactions. The chain prolongation rate is proportional to the concentration of the reagent which takes part in the chain prolongation. Thus $G(-O_2)$ must be in linear dependence on [RSH] or on $[O_2]$, or $G(-O_2)$ will depend on both concentrations. As is seen from fig., the linear dependence of [RSH] is not realized in a whole pH range. In other experiments we have established that $G(-O_2)$ does not depend on $[O_2]$ when O_2 is not in competition with RSH for a solvated electron. The next experiment confirms that the loss of O_2 in radiolisis is not caused by reactions of (1 — 3) type offered by previous investigators.

$$RSH + OH^\circ \rightarrow RS^\circ, \quad (1)$$

$$RSH + H^\circ \rightarrow RS^\circ, \quad (2)$$

$$RS^\circ + O_2 \rightarrow RSOO^\circ \rightarrow \text{products of oxidation.} \quad (3)$$

In this experiment the RS° radicals were generated in the solution by a non radiation method. In [1] and other works it is shown that the O_2^- radical reacts with RSH in reactions (4, 5).

$$O_2^- + RSH \rightarrow HO_2^- + RS^\circ, \quad (4)$$

$$2RSH + H_2O_2 \rightarrow RSSR + H_2O. \quad (5)$$

In our previous experiments we obtained the value of the rate constant in the case of 2-aminoethanethiol. $K_4 = (7 \pm 4) \cdot 10^2 m^{-1} c^{-1}$. The gradual injection of 0_2^--ions into a solution of RSH will cause the formation of RS° radicals in the solution. Such a solution does not contain any other products besides those formed in the radiolysis. In the experiment the electrons formed in a helium discharge were drawn into the air by the electric field, forming 0_2^-. The 0_2^- ions moving in the electric field came upon the aerated solution of RSH. The solution was mixed with a stirrer. In control experiments it was shown that 90% of the current in such installations is due to 0_2^--ions [6].

Table 1

[RSH] (M)	10^{-3}	$5 \cdot 10^{-4}$	$2 \cdot 10^{-4}$
$\frac{\Delta[RSH]}{[0_2^-]}$	3.6	2.8	2.5

Table 2

[RSH] (M)	10^{-3}	$5 \cdot 10^{-4}$	$2 \cdot 10^{-4}$
G(—RSH)	58	43	24

Table 1 gives the relation of the SH — group decay to the total amount of 0_2^- injected in the solution (pH = 9,1 tetraborate). As is seen from table 1 thiole decays only in reactions (4) and (5). And there is no additional oxidation by dissolved oxygen. This experiment confirms the assumption [7] that RS° radicals decay only in reactions (6) and (7).

$$RS^\circ + 0_2 \rightarrow RSO_2^\circ , \tag{6}$$

$$RSO_2^\circ + RSO_2^\circ \rightarrow RSSR + 2O_2 . \tag{7}$$

To compare table 2 gives values of the radiation yields of SH-group losses when 2-aminoethanethiol is irradiated in the same conditions. (^{137}Cs source, Dose rate 52 rad/min). This dose rate provided the rate of formation of water radicals (which are then converted to RS° radicals in reactions with RSH) equal to the rate of 0_2^--ions entering in the previous experiment given in table 1. The total yield of water radicals is ≈ 6. The solution is diluted enough to exclude the direct action of radiation. Thus it is clear that G(—RSH) may be explained only by considering the dissolved oxygen involved in the reactions.

We explain the data given above and other data by the mechanism in which we suppose there is a formation of thiole molecules in the electron excited state [6]. The formation of excited molecules in relatively low thiol concentrations, when the direct action of radiation is small, may be possible in unelastic collisions of low energy electrons with molecules of thiol.

When the electron energy becomes lower than the energy of the lower excited state of water molecule, the rate of energy losses by electron becomes sharply reduced. This electron before thermolisation suffers a large number of collisions with the molecules of solution [8]. And it may incounter the RSH molecule even at low thiol concentrations.

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