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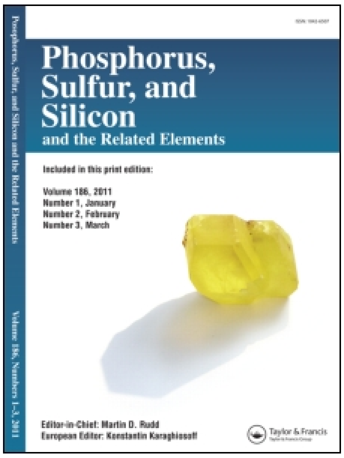

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RADIATION CHEMISTRY OF AMINOALKYITHIOIS

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RADIATION CHEMISTRY OF AMINOALKYLTHIOLS

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Radiation chemistry of aminoalkylthiols and some derivatives (aminoalkyl-S-thiophosphates and aminoalkyl-S-thiosulfates among which are most effective radioprotectors) in aqueous solutions has been studied in order to establish the relation between the structure of these compounds and their radiation-chemical properties. Increase in the number of methylene groups between the sulfur atom and nitrogen atom in the aminothiol molecule from 2 to 4 and substitution of the amino group hydrogene by an alkyl radical has been found to be without appreciable effect both on the "spectra" of radiolisis products and rate constants for interaction of H, e_{aq}^- and OH with aminothiols

Radiation-chemical behaviour of aminothiols strongly depends on solution pH, i.e. on protonation state of both functional groups in aminothiols. In acid and neutral solutions, where thiols are in protonated form (RSH) the radicals e_{aq}^- and OH are known to attack the -SH group according to the following reactions:

$$RSH + e_{aq}^- \longrightarrow R\cdot + SH^- \qquad (1)$$

$$RSH + OH \longrightarrow RS\cdot + H_2O \qquad (2)$$

Deprotonation of -SH group in aminothiols moleculs such as 2-aminoethanethiol, 3-aminopropanethiol, cystein, homocystein and glutathion has been shown to be accompanied by e_{aq}^- attack of the positively charged amino group rather than S^- group. The product of this reaction is ammonia:

$$H_3NRS^- + e_{aq}^- \longrightarrow {}^\bullet RS^- + NH_3 \qquad (3)$$

The $\bullet RS^-$ radical produced is reduced to thiolate anion RS^-. Thus there is evidence for building up of thiopropionic acid at cystein radiolisis at pH 10.

The curve relating the ammonia yield and pH is bell-shaped and agrees with the per cent number of zwitterion form of aminothiols (H_3NRS^-) as a function of pH. The radiolisis of 4-aminobutanethiol fails to result in ammonia production for in this case $pK_{SH} \approx pK_{NH_3^+}$.

In the presense of oxygen radiation oxydation of aminothiols over pH range 3 to 7 does not stop at disulfide production, the product being sulfonic acids. The chain reactions do not occur at low aminothiols concentration (10^{-4}M) at pH 3 to 8, in the presence of oxygen.

Other is the picture of radiolisis when the hydrogen of -SH group in aminothiols is substituted by residues of phosphoric or sulphuric acids, i.e. with aminoalkyl-S-thiophosphates and aminoalkyl-S-thiosulphates. Thus, unlike aminothiols, no disulfides have been observed among radiolisis products. On the other hand, there have been detected formerly unknown thiophosphoric compounds with general formula $RSSPO_3H_2$.

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