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TITLE: The utilization of an induced iodine-azide reaction for the investigation of changes in sulphur aminoacids under the influence of ultraviolet light

SOURCE: Poznan. Uniwersytet. Zeszyty naukowe. no.40. Matematyka, fizyka, chemia. no.6. 1962. 3-11

TEXT: The investigation was carried out in order to study changes in cystine and cysteine in solutions under the influence of ultraviolet light using iodine-azide induced reaction for the determination of the above aminoacids.

$R\text{-}SH + I_2 \rightleftharpoons R\text{-}S\text{-}I + HI$; $R\text{-}S\text{-}S\text{-}R + I_3^{\bullet} \rightleftharpoons 2\,R\text{-}S\text{-}I + I^{\bullet}$.

In acid solutions $R\text{-}S\text{-}I + N_3^{\bullet} \longrightarrow R\text{-}S\text{-}N_3 + I^{\bullet}$, the $R\text{-}S\text{-}N_3$ formed reacts with $I\text{-}N_3$ (formed in acid solution):

$R\text{-}S\text{-}N_3 + I\text{-}N_3 \longrightarrow R\text{-}S\text{-}I + 3\,N_2$, the reaction continues until, due to side reactions, the mercaptan is irreversibly oxidized, e.g. to sulphonic acid which does not induce this reaction.

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Irradiated solutions of cystine at pH 8 become yellow. Samples analysed in the course of irradiation indicated that the amount of cystine decreases while the amount of cysteine increases, attaining in time (3 to 5 hours) a constant value of about 30%. Simultaneous decrease in cystine was higher than the amount of cysteine formed. The latter indicated the formation of another substance, probably cysteic acid which does not induce iodine-azide reaction. Beginning from the 5th hour of the irradiation, an equilibrium between the sum of cysteic acid and cystine and cysteine became established. During the reaction some decrease in pH (0.2 to 0.4 units) was observed, indicating the appearance of a stronger, probably sulphonic, acid. The results obtained on irradiation of a solution of the mixture of cysteine and cystine in the ratio of 1:3 indicated that the original level of cysteine is maintained, while that of cystine decreased. On irradiation of a solution containing only cysteine, the formation of cystine and a decrease in cysteine was observed, whereupon the level of cysteine stabilizes at a value of 28% of the original concentration. On irradiation of cystine in acid solutions (pH 2 to 5) the

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precipitation of colloidal sulphur takes place. The formation of H_2S as an intermediate product was observed. The precipitation of sulphur can be prevented by the addition of formaline. There are 4 figures.

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