The X-Radiolytic Destruction of Lipoic Acid In Aqueous Solution; A Chain Reaction

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IRRADIATION of aerated aqueous solutions of 6-thioctic acid (α-lipoic acid), concentration 0·4 to 8·3 mM, pH 3·5 to 5·0, with 125 kVp X-rays at a dose rate of 3565 rads. min.$^{-1}$ produced a progressive diminution in the absorption (λ_{max} 330 mμ) of the dithiacyclopentane chromophore. Absorption below 290 mμ increased concomitantly, eventually with the production of a shoulder at 240—245 mμ and demonstration of an isosbestic point at 294 mμ, which was sharp at least up to destruction of one third of the lipoate initially present. Initial rates, G_0, of disappearance, obtained from the tangents at zero time to the yield–dose curves, were markedly concentration dependent and unusually high, ranging from 4·8 to 25·8 molecules per 100 ev over the concentration range studied. The concentration-dependence is non-linear (Figure a) but a log–log plot (Figure b) indicates the relationship G_0 (-lipoate) = 360 [lipoate]$^{0\cdot55}$. Very similar observations resulted from a less extensive study of deaerated solutions irradiated under argon.

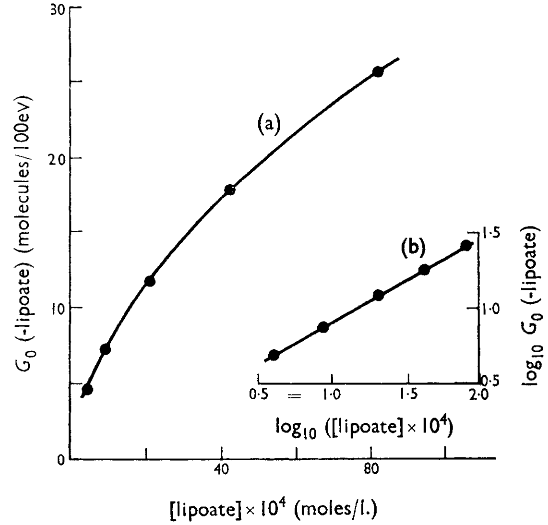

FIGURE.

Effect of lipoate concentration on G_0 (—lipoate).

The magnitude of G_0 (-lipoate) is notable; at the highest concentration here reported it is several times larger than $G_H + G_{OH} + G_{H_2O_2}$ and six to twenty times as great as the typical yields for destruction of acyclic disulphides[1,2] in aerated aqueous solution. Direct interaction of incident radiation with solute ("direct effect") is improbable at solute concentrations below 10 mM. We conclude that lipoate destruction occurs by a chain reaction, possibly polymerization. Such chain reaction has not, to our knowledge, been reported previously for the radiolytic destruction of disulphides in aqueous systems. Polymerization has been suggested to account for destruction of lipoic acid photolytically[3] and upon β- or γ-radiolysis in hexane[4] and the ultraviolet spectrum of our radiolysis product is quite similar to that of the product of photolysis[3] and to those of acyclic disulphides. The absence of an oxygen effect vitiates suggestion of a stoicheiometric oxidation product such as a monosulphoxide.[3]

Interpretation of the mechanism of the chain reaction awaits further investigation, particularly of the nature of the products of radiolysis. Initiation by $\cdot$OH probably involves electron abstraction to give a disulphide radical-cation. Similar reaction of $\cdot O_2H$ is possible but this suggestion is disallowed by the absence of any oxygen effect, and initiation by $\cdot$H or e^-_{aq} giving a radical-anion is a likely alternative, especially in those solutions in which the concentration of disulphide considerably exceeds that of oxygen. The unusual reactant exponent, ~0·5, suggests propagation and termination by a Rice–Herzfeld mechanism[5] with at least two chain carriers and second-order chain breaking. More usual kinetics, requiring first-order or greater reactant dependence, are clearly untenable.

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