THE ENZYMATIC HYDROLYSIS OF TRIPROPIONYL GLYCEROL, TREATED AS A CONSECUTIVE REACTION

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Recent experiments[1] have suggested that in the hydrolysis of tripropionyl glycerol (tri) by liver esterase there are produced two intermediate products, 1,2-dipropionyl glycerol (di) and 2-monopropionyl glycerol (mo), and that the processes tri $\rightarrow$ di (I), di $\rightarrow$ mo (II) and mo $\rightarrow$ gl (III) proceed at extremely different rates. Investigations have now shown that (I), (II) and (III) may proceed according to the mechanism which is given below. By varying the substrate concentrations of tri, di and mo, it is possible on the basis of the reaction curves to compute the numerical values of all the k-values (with the exception of k_{-5}) in relation to the same enzyme concentration which is put = 1. We have then suggested the following reaction scheme for the consecutive reactions in the degradation of tripropionyl glycerol:

$$\left.\begin{aligned} OH^- + \text{tri} + X_1 &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X_2 + P^- \\ X_2 &\xrightarrow{k_2} X_1 + \text{di} \end{aligned}\right\} \text{I}$$

$$\left.\begin{aligned} OH^- + \text{di} + X_1 &\underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} X_3 + P^- \\ X_3 &\xrightarrow{k_4} X_1 + \text{mo} \end{aligned}\right\} \text{II}$$

$$\left.\begin{aligned} OH^- + \text{mo} + X_1 &\underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} X_4 + P^- \\ X_4 &\xrightarrow{k_6} X_1 + \text{gl} \end{aligned}\right\} \text{III}$$

where $X_1 \ldots X_4$ are different forms of liver esterase, P^- = propionic acid, gl = glycerol. The OH^--concentration which is kept constant during the hydrolysis[2] does not enter in the mathematical treatment. Assuming a stationary state for each of the reactions I, II and III, and $k_{-1}/k_2 = k_{-3}/k_4 = k_{-5}/k_6$, it is possible to solve the differential equations of the three consecutive reactions. Integration of these differential equations leads to the following parameter description:

$$Et = A \ln \frac{a}{a-x} + Bx + C\left[1 - \left(\frac{a-x}{a}\right)^{k_I}\right] + D\left[1 - \left(\frac{a-x}{a}\right)^{k_{II}}\right] \qquad (1a)$$

and

$$U = a\left[3 - K\left(\frac{a-x}{a}\right) - L\left(\frac{a-x}{a}\right)^{k_I} - M\left(\frac{a-x}{a}\right)^{k_{II}}\right] \qquad (1b)$$

where A, B, C, D, K, L, M, k_I and k_{II} are expressed by means of the velocity constants and a (initial concentration of tri), whereas x (degraded tri) is the parameter. U = amount of acid liberated from tri, di and mo at time t. E = enzyme concentration. By inserting the values of the velocity constant in (1a) and (1b) a very good agreement is found between the experimental and calculated values of U and t. This indicates that the mechanism suggested may be correct.

REFERENCES

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