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Kinetic Study on the Release of Thiamine Disulfide (TDS) from TDS-Higher Fatty Acids Complexes. II. Effect of Odd-Numbered Fatty Acids*

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The rates of release of thiamine disulfide (TDS) from odd-numbered fatty acids-TDS complexes, $(C_{2n-1})_6$ (TDS), were determined at various temperatures, and the thermodynamic quantities in the kinetics for the release of TDS from the complexes were estimated.

The rate of release of TDS from the complexes decreased with increasing carbon number in the odd-numbered fatty acid and increased at a higher temperature. The values of activation Gibbs energy ΔG^{\pm} and activation enthalpy ΔH^{\pm} for the release of TDS from the complexes were positive. The value of activation entropy ΔS^{\pm} was negative.

The results obtained for $(C_{2n-1})_6$ (TDS) were compared with the previous results obtained for the even-numbered fatty acids-TDS complexes, $(C_{2n})_6$ (TDS). The plots of the release rate constant of TDS from the complexes against the carbon numbers of the constituent fatty acids showed a zig-zag pattern which indicates a downward convex at an odd-numbered position. Furthermore, the plots of the positive values of ΔH^{\pm} against the carbon numbers of the constituent fatty acids showed a zig-zag line which indicates an upward convex at an odd-numbered position, while the plots of the negative values of ΔS^{\pm} showed a zig-zag line which indicates a downward convex at an odd-numbered position. The release of TDS from $(C_{2n-1})_6$ (TDS) is more disadvantageous from the activation enthalpic viewpoint and more advantageous from the activation entropic viewpoint than $(C_{2n})_6$ (TDS). It is found that the release of TDS from $(C_{2n-1})_6$ (TDS) is an enthalpically controlled reaction, making the release more disadvantageous due to the enthalpic effect. The zig-zag line for the release rate of TDS from the complexes can be explained by the thermodynamic parameters of the transition intermediate.

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