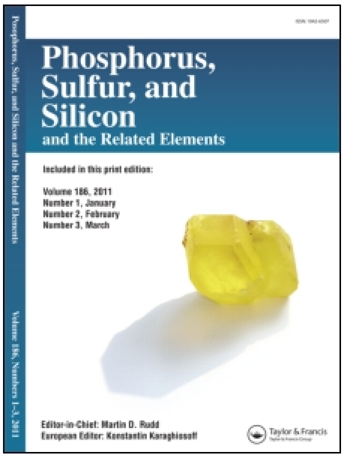

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THE NATURE OF INTERMEDIATES OF ISOMERISATION AND OF NUCLEOPHILIC SUBSTITUTION OF β-CHLOROALKYLTHIOCARBOXYLIC ACID DERIVATIVES

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THE NATURE OF INTERMEDIATES OF ISOMERISATION AND OF NUCLEOPHILIC SUBSTITUTION OF β-CHLOROALKYLTHIOCARBOXYLIC ACID DERIVATIVES

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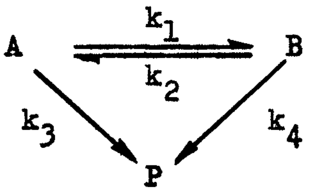
The addition of sulfenchlorides to the derivatives of unsaturated carboxylic acids results in the formation of kinetically controllable adducts, which in solution and even in a solid state isomerize into thermodinamically stable ones. The derivatives of β-chloroalkylthiocarboxylic acids readily enter nucleophilic substitution reactions, particularly the reaction of hydrolytic splitting of C-Cl bonding. There still remains a problem to be solved concerning the nature of the intermediates which appear in the process of isomerisation and hydrolysis of these compounds. To solve the problem the research was carried out on the effect of chlorine and perchlorate ions concerning the rate of hydrolysis and isomerisation of the derivatives 2(3)-chloro-3(2)-alkylthio-2-methylpropanoic acids.
The reactions were performed in dioxane and water mixtures containing 66.7 and 14.3% organic solvent. Kinetic data were obtained from the analysis of PMR spectra of partial hydrolysis of compounds. The overall kinetic scheme including the



Reaction scheme

transformation of original chloroderivatives (A,B) as well as the formation of the products of substitution (P), was evaluated by means of a computer. Kinetic constants were calculated applying the local searching method.

The results obtained showed that the isomerisation of chloroderivative compounds in 66.7% solution exceeded the rate of hydrolysis by more than the order of two. Velocity constants of isomerisation (k_1) of unstable 3-chloroderivative isomers are 3.8-5.3 times higher than those (k_2) of stable 2-chloroderivatives. The ratio of hydrolysis constants (k_3, k_4) of isomers comes up to 16-31. The velocity constants of isomerisation remain practically unaffected by adding lithium chloride (0.2 M) to the solution. Whereas the velocity constants of hydrolysis decrease by the factor of 2.7-5.0. It follows that the chlorine ions decelerate hydrolysis without effecting the isomerisation. The effect is due to the chlorine ions, since the ions of perchlorate result in some accelaration of hydrolysis.

Competitive factor was determined in 14.7% aqueous dioxane by means of pH-stat. In the case of stable 2-chloroderivatives it is equal to 11.7 M^{-1} or less than 0.15 M^{-1} for chlorine and perchlorate ions respectively.

In the light of the data obtained we can draw the couclusion that in nucleophilic substitution reactions a dissociated intermediate - episulphonium ion is formed. The structure of episulphonium ions remains the same both for 2- or 3-chloroderivatives. In case of isomerisation the dissociated intermediate is not formed. It is being assumed that in such an intermediate the chlorine atom and alkylthiogroup interact simultaneously with 2- and 3-atoms of carbon. Such an intermediate can be of an extremely low stability.