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Influence of Substituents in Position 5 on the Kinetics of Chlorine Isotope Exchange Reaction in 5,5-Disubstituted 2-Chloro-2-oxo-1,3,2-dioxaphosphorinanes and their Thioanalogues

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Influence of Substituents in Position 5 on the Kinetics of Chlorine Isotope Exchange Reaction in 5,5-Disubstituted 2-Chloro-2-oxo-1,3,2-dioxaphosphorinanes and their Thioanalogues

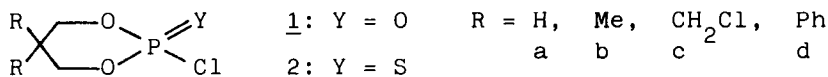
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Cyclic phosphates are a great interest as a result of their biological importance. The kinetics of nucleophilic substitution at phosphorus atom in these compounds has not been studied thoroughly.

This communication presents the rate constants of chlorine isotope exchange between $^{36}\text{Cl}^-$ and 5,5-disubstituted 2-chloro-2-oxo-1,3,2-dioxaphosphorinanes 1 and their 2-thioanalogues 2 in dilute acetonitrile solutions at temperatures of 25 - 75° C.



A strong influence of the substituents on the rate constants of exchange reaction has been observed. For both series of phosphates 1 and 2 the values of k_1 and k_2 increase in following order $k_d < k_b < k_a < k_c$. The value of k_c is greater than k_d over 300 times. However, no influence of substituents has been observed on the ratio of rate constants for reactions of phosphates and thio-phosphates.

The mechanism of nucleophilic substitution is proposed. It seems that two intermediates P^{V} of different ring conformation play an important role in this mechanism.