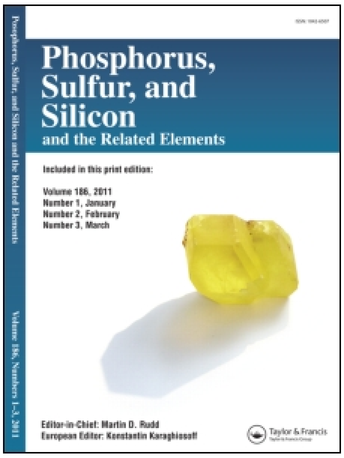

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Kinetics and Mechanism of the Insertion Reaction of Arylisocyanates into C-C Bond of Phosphabetaine Obtained ont the Basis of Triisopropylphosphine and 2-Cyanoethylacrylate

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Kinetics and Mechanism of the Insertion Reaction of Arylisocyanates into C-C Bond of Phosphabetaine Obtained on the Basis of Triisopropylphosphine and 2-Cyanoethylacrylate

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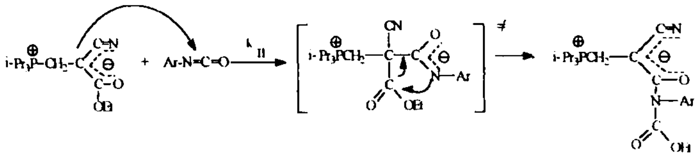
On the basis of kinetic investigation of previously discovered [1] insertion reaction of arylisocyanates into C-C bond of zwitter-ions, obtained on the basis of trialkylphoshines and 2-cyanoacrylates, the mechanism of this unusual reaction has been suggested. According to this mechanism the nucleophilic attack of zwitter-ion anionic center on the carbon atom of isocyanate group and nucleophilic attack of nitrogen atom on carbethoxylic group, leading to breakup of C-C bond, carry out relatively synchronously within one transition state on the concerted mechanism.



The driving force of migration of carbethoxylic group to the nitrogen atom may be conditioned by steric hindrance in transition state and also by energy advantage from more effective delocalization of anionic charge in the forming product.

Such a mechanism is confirmed by high negative values of activation entropy and by expressed influence of substituents in aromatic ring of arylisocyanates (reaction rate changes ~ in 1000 once).

The mechanism suggested is also in a good agreement with solvent influence on the reaction rate, which has been studied in the framework of Koppel-Palm approach.

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[1] Gololobov Yu.G., Kardanov N.A., Khroustalyov V.N., Petrovskii P.V. Tetr.Lett., 1997, **38**, 7437.