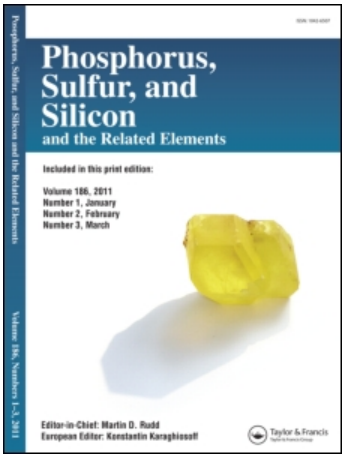

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KINETIC ENANTIOSELECTIVITY IN THE ALKANESULPHONYL AMIDES FORMATION REACTION

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KINETIC ENANTIOSELECTIVITY IN THE ALKANESULPHONYL AMIDES FORMATION REACTION

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In order to obtain quantitative information on the non-bonded interactions in the formation of alkanesulphonyl amides, the kinetics of the reaction between (-)-camphor-10-sulphonyl chloride and (-)- and (+)-1-phenylethylamine (1-PhEtA) in benzene, chlorobenzene, chlorobenzene-nitrobenzene mixtures (1, 4 and 11 v.% of the latter), in a chlorobenzene-o-dichlorobenzene mixture (50v.%) and in o-dichlorobenzene have been studied. The reaction proceeds by two parallel pathways: by a non-catalytic one, and by a initial amine-catalized one. The enantioselectivity of the non-catalytic pathway, estimated by the ratio of the fast reacting enantiomer rate constants ((+)-1-PhEtA) to those of the slowly reacting one ((-)-1-PhEtA) has the following values in various solvents: 1.32 (benzene), 2.27 (chlorobenzene), 2.09 (1v.% of nitrobenzene in chlorobenzene), 2.55 (4v.% of nitrobenzene in chlorobenzene), 3.76 (11v.% of nitrobenzene in chlorobenzene), 1.43 (50v.% of o-dichlorobenzene in chlorobenzene) and 1.05 (o-dichlorobenzene). Data on the kinetic enantioselectivity of the initial amine-catalyzed pathway which is smaller in all the media than the enantioselectivity of the non-catalyzed pathway have also been obtained.
From the data obtained it has been concluded that the reaction in point proceeds by the mechanism of nucleophilic substitution at the sulphur atom.