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A Simpe Model for the Description and Prediction of the Thermodynamic Substrate and Regioselectivities of Alkane CH Activation with Metal Complexes

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Abstract

The empirical Pauling equation was used to develop a simple qualitative model for the description and prediction of the thermodynamic substrate and regioselectivities of alkane reactions with carbenes, nitrenes, oxene, halogens, and metal complexes. The feasibility of the model was demonstrated on examples of isomerization and transfunctionalization reactions of alkyl halides, alcohols, thiols, primary amines, and nitro compounds. A sequence of thermochemical electronegativity of simple alkyl radicals is proposed. The thermodynamic selectivity of reactions of alkanes and benzene with metal complexes was examined in terms of the developed model. It is shown that the electronic factor controlling the type of selectivity operates in a direction that depends on the electronegativity ratio between the metal-complex group attached to organic radical (χM) and hydrogen (χH). On the basis of published thermodynamic data for alkyl and phenyl derivatives of Group IV, VII, IX, X, and XII metals, the possibility of correctly predicting the substrate and regeoselectivities of hydrocarbon reactions with these compounds was substantiated.