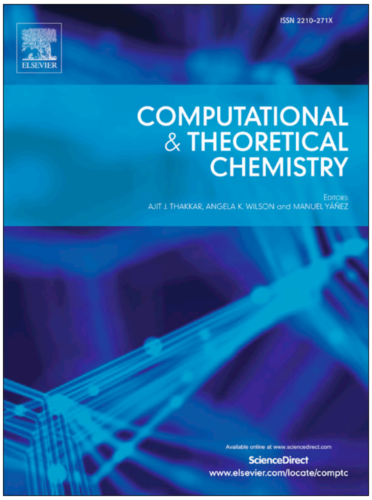

Study of gas-phase reactions within the modified Marcus model. I. CH4 + CH3 → CH3 + CH4

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Study of gas-phase reactions within the modified Marcus model. I. $CH_4 + CH_3 \rightarrow CH_3 + CH_4$

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ABSTRACT: The temperature dependence (temperature range10 - 800 K) of the rate constants, *k*, of gas-phase reactions of the transition of hydrogen and deuterium atoms from methane to the methyl radical was studied within the framework of the Marcus theoretical model. The value of *k* at the temperature T, *k*(T), is defined as the integral over the distance Q between the C atoms of the reagents in the activated complex (AC). The activation parameters of the reaction were calculated using the previously proposed method of direct ab initio calculation (the method of intramolecular reorganization (IMR)). The calculation level was UCCSD(T)/6-311++G**//B3LYP/6-31+G**. Two possible system oscillation models in AC were considered. In the first (model 1) all system vibrations ars considered real, while in the second (model 2) the standard TST treatment with one imaginary vibration is used. Model 1 demonstrates the best agreement with experiment. The plot 1/T - lg*k* has nonlinear (80 – 800 K) and linear (10 – 80 K) parts. Factors causing the non-Arrehenius rate constant behavior are considered. A relationship between the kinetic dependence at low temperatures and the “temperature plateau” phenomenon, observed the study of the kinetics of hydrogen atom transfer reactions in solid phase, is noted.

Keywords: Arrhenius equation, structure coordinate, tunneling, KIE.

1. INTRODUCTION

The use of proton coordinate as a structural reaction coordinate, proposed in the intramolecular reorganization (IMR)[1] method, provides an opportunity for the direct ab initio calculations of activation parameters of proton transfer reactions in the framework of the Marcus theoretical model[2, 3]. This approach has previously been used to analyze of the Broensted relation[4]. The present work investigates the kinetics of a gas-phase hydrogen transfer reaction using this