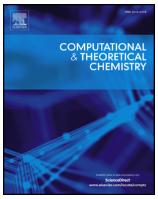
Computational and Theoretical Chemistry 1138 (2018) 66–74

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc



Study of gas-phase reactions within the modified Marcus model. II. $CH_3OH + CH_3 \rightarrow CH_2OH + CH_4$

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ARTICLE INFO

Keywords:
Arrhenius equation
Tunneling
Gas-phase reaction
Solid-phase reaction
"Temperature plateau" phenomenon

ABSTRACT

In the framework of the Marcus theoretical model, using the intramolecular reorganization (IMR) method, the kinetics of the $CH_3OH + CH_3 \rightarrow CH_2OH + CH_4$ reaction was studied over the temperature range of 10–550 K. The electronic activation energy (E_a) was calculated at the UCCSD(T)/6-31 + G**//B3LYP/6–31 + G** level. The calculation of the reaction rate constant, k, defined as the integral over the distance Q(C···C), was carried out on the assumption that for a hydrogen atom in the activated complex (AC) two extreme types of vibrations are possible: isolated vibration in the reagent well (oscillatory model 1, in which all frequencies are identified as real) and vibration in the C···H···C structure (oscillatory model 2 corresponding to TST). In both cases, the temperature dependence of the rate constant includes nonlinear (80–550 K) and linear (10–80 K) sections. It is shown that the change in the dependence character is due to the presence of a minimum in the Q - E_a plot. Kinetic data were used to analyse the "temperature plateau" phenomenon, observed for the $CH_3OH + CH_3$ reaction in the solid phase. The course of the temperature dependence of this reaction at 10–150 K can be reproduced assuming that the energy of the reagents in the solid phase is close to the average for the effective interval Q of the enthalpy of activation of the gas-phase reaction, $\Delta H_m{}^*$, in a temperature range of 10–40 K. The value of the deuterium KIE for model 1 is ~10^4, which is about an order of magnitude higher than the experimental value.

1. Introduction

Previous research [1] was devoted to the analysis of the kinetics of the reaction methane with the methyl radical:

$$CH_4 + CH_3 \rightarrow CH_3 + CH_4 \quad (1)$$

The analysis was conducted in the framework of the Marcus theoretical model [2,3] with the use of the intramolecular reorganization (IMR) technique [4]. In this paper, we use this approach to consider of the reaction of H and D atoms abstraction from the methyl group of methanol by the CH_3 radical:

$$CH_3OH + CH_3 \rightarrow CH_4 + CH_2OH \quad (2)$$

$$CH_2DOH + CH_3 \rightarrow CH_3D + CH_2OH \quad (3)$$

Information on the kinetics of Reactions (2) and (3) at 350–550 K is given in the review of Moss and Kerr [5]; the activation energies, E_{act}, for H and D atom abstraction were reported to be 10.0 (± 1) and 11.3 (± 2) kcal/mol, respectvely. In accordance with interest in methanol combustion mechanism, studies into the kinetics of Reaction (2) were also carried out at high temperatures (1600–2100 K) [6]. Empirical relationships describing the dependence of the rate constants of Reaction (2) in the 300–2000 K temperature range are given in Tsang's review [7]. Iodkovsky [8] and Truhlar [9,10] showed that these data are satisfactory when described within canonical TST.

The kinetics of Reaction (2) in the condensed phase (frozen methanol) reveals a pronounced non-Arrhenius behavior. At temperatures of approximately 100 K, $E_{act} \approx 1$ kcal/mol, and at lower temperatures, this value approaches zero [11,12]. This fact, as well as the very high deuterium isotopic effect (~1000 at 77 K) [13] indicates that tunneling is a dominant kinetic factor. In theory [14,15], the "temperature plateau" phenomenon is associated with the specificity of the hydrogen atom transition reaction in the solid phase; it is assumed that the decrease in E_{act} is due to the activating role of low-frequency vibrations of heavy atoms in the crystal lattice.

Tachikawa et al. [16] attempted to explain the features of the solid-phase process using a description of the gas-phase reactions kinetics. The discussion was carried out within the framework of the RRMM theory with the inclusion of tunneling effects (the Miller modification). Along with tunneling through the saddle point along the lowest energy path, alternative routs are considered - tunneling along the lines connecting the isoenergetic points in the reagent and product channels on

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https://doi.org/10.1016/j.comptc.2018.04.010
Received 13 January 2018; Received in revised form 20 March 2018; Accepted 20 April 2018

the two-dimensional equilibrium PES. At temperatures below 100 K, the second path is preferred. Through energy scaling (in relation to the experimental E_{act}), it is possible to describe the horizontal range of the rate constant temperature curve, as well as the magnitude of the observed KIE.

The purpose of this paper is to examine the kinetics of gas-phase Reactions (2) and (3) within the framework of the modified Marcus model [4]. The used IMR method allows for the direct ab initio calculation of the geometry and the potential energy of the reaction AC. These data are then used to calculate the free-energy activation parameters and the absolute reaction rate constant. Due to the relatively large size of the system (in comparison with Reaction (1)), the basis set in the ab initio calculations was reduced (see Section 3). The investigated temperature interval (10–550 K) includes regions in which experimental measurements of the gas- and solid-phase kinetics were made. Despite the high exothermicity of Reaction (2), it was found that the general laws of the gas phase reaction as a whole are similar to those observed for the thermoneutral Reaction (1). At low temperatures, the Arrhenius plot for the gas-phase reaction has a nonzero slope. The possibility of analyzing the "temperature plateau" phenomenon observed for solid-phase kinetics based on these data is considered in this article.

2. Theory

2.1. The IMR method

According to the theory of nonequilibrium reactions, the PT reaction includes the steps of (1) movement of the reagents closer to a certain center-to-center distance Q; (2) system reorganization, i.e., motion of the system along the structural coordinate q at constant Q (the system potential V(q|Q)); and (3) proton tunneling for fixed values of q^* and Q in the symmetric potential $V(r|q^*,Q)$, where r is the coordinate of the proton and q^* is the value of the coordinate q, corresponding to the symmetrization of the potential V(r|q,Q).

In the IMR method, the use of proton coordinate r as the structural coordinate of the reaction is recommended. In connection with this, it is assumed that the system motion along r is infinitely slow. For the description of this slow motion in particular, an additional coordinate ρ (geometrically identical to coordinate r) is introduced. The motion along coordinate ρ, like the motion along q, is accompanied by system reorganization at constant Q. There is a one-to-one relationship between the equilibrium potentials V(q|Q) and V(ρ|Q): each point on coordinate q can be associated with a definite point on coordinate ρ and vice versa. This correspondence allows us to replace the multidimensional coordinate q by the one-dimensional coordinate ρ. As a result, the direct ab initio calculation of the geometry (and energy) of the AC becomes possible using standard computational software packages such as GAUSSIAN.

In the framework of this approach, the system potential in the tunneling stage, $V(r|\rho^*,Q)$, where ρ^* is coordinate ρ at the moment of the potential V(r|ρ,Q) symmetrization, can be represented as:

$$V(r|\rho^*, Q) = V_{\mathrm{eq}}(\rho = r|Q) + V_{\mathrm{neq}}(r|\rho^*, Q) \tag{4}$$

where $V_{eq}(\rho = r|Q)$ is the energy corresponding to the slow motion of the system along coordinate r, i.e., at $\rho = r$ (the potential $V_{eq}(\rho = r|Q)$ is identical to the potential $V(\rho|Q)$, $V_{eq}(\rho = r|Q) \equiv V(\rho|Q)$ and $V_{neq}(r|\rho, Q)$ is the nonequilibrium contribution associated with the fixation of coordinate ρ. The potentials $V_{eq}(\rho = r|Q)$ and $V(r|\rho^*,Q)$ are shown in Fig. 1.

At the point of the left minimum, i.e., at $r = r_{01}$, the energy $V(r|\rho^*, Q)$, $V(r_{01}, \rho^*, Q)$, is equal to:

$$V(r_{01}, \rho^*, Q) = V_{eq}(r_{01}, Q) + V_{neq}(r_{01}, \rho^*, Q) \tag{5}$$

or in abbreviated form:

$$V^* = V_0 + (V^* - V_0) \tag{6}$$

where $V^* = V(r_{01}, \rho^*, Q)$ *and* $V_0 = V_{eq}(r_{01}, Q)$ (It is assumed that the positions of the minima in the potentials V^* and V coincide). In accordance with Eq. (6), the electronic activation energy of the reaction, E_a, can be represented as the sum of the equilibrium, E_a^{eq}, and nonequilibrium, E_a^{neq}, contributions[1]:

$$E_a = E_a^{eq} + E_a^{neq}, \tag{7}$$

$$E_a^{eq} = V_{01} - V_{reag} \tag{8}$$

$$E_a^{neq} = V^* - V_{01} \tag{9}$$

where V_{reag} is the energy of the initial reagents, V_{01} is the energy of the left minimum in the potential $V_{eq}(\rho = r|Q)$ and V^* is the energy of the left (right) minimum in the $V(r|\rho^*,Q)$ potential.

As preliminary calculations have shown, in the case of Reactions (2) and (3), the positions of the left minima of the potentials $V_{eq}(\rho = r|Q)$ and $V(r|\rho^*,Q)$ do not coincide. For this reason, the V_{01} energy was not calculated (and, correspondingly, the E_a^{eq} and E_a^{neq} energies), limiting ourselves to calculating the energy E_a by the equation:

$$E_a = V^* - V_{reag} \tag{10}$$

Other energy parameters, including the reaction energy, ΔE_{00}, the "internal reaction energy" (for the collision complex), ΔE_0, and the height of the central barrier in the potential $V(r|\rho^*,Q)$, E_b, were found from the relations 11, 12 and 13, respectively.

$$\Delta E_{00}^0 = V_{\mathrm{prod}} - V_{\mathrm{reag}} \tag{11}$$

$$\Delta E_0 = V_{02} - V_{01} \tag{12}$$

$$E_b = V^\# - V^* \tag{13}$$

where V_{prod} - is the energy of the products, V_{02} is the energy of the right minimum in the potential $V_{eq}(\rho = r|Q)$ and $V^\#$ is the energy at the top of the barrier in the $V(r|\rho^*,Q)$ potential. The aforesaid is illustrated by Fig. 1.

2.2. Rate constant

The calculation of the rate constant of the bimolecular Reactions (2) and (3) at a given temperature T(K), k(T), was carried out using Eqs. (14a)–(14e) [2,17,18].

$$k(T) = \sigma \int k(Q) = \sigma \int \nu_t(Q) exp(-\Delta G^*(Q)/RT)dQ \tag{14a}$$

$$\Delta G^*(Q) = \Delta H^*(Q) - T\Delta S^*(Q) \tag{14b}$$

$$\Delta H^*(Q) = E_a(Q) + \Delta h^*(Q) \tag{14c}$$

$$\Delta S^*(Q) = [\Delta h^*(Q) - \Delta g^*(Q)]1000/T \tag{14d}$$

$$\Delta h^*(Q) = h^*(Q) - h, \quad \Delta g^*(Q) = g^*(Q) - g \tag{14e}$$

where σ is the symmetry number (for Reactions (2) and (3) $\sigma = 3$); ν_t is the tunneling frequency, ΔG^*, ΔH^* and ΔS^* are the free energy, enthalpy and entropy of activation, respectively; Δh^* and Δg^* are the thermal corrections to the enthalpy and the free activation energy, respectively, where $h^*(h)$ and $g^*(g)$ are the corresponding thermal corrections (taking into account zero point vibrational energies) for the AC (reagents) and R is the gas constant (1.987 kcal/mol·grad). The calculation of the thermodynamic parameters was carried out in the rigid rotor approximation without accounting for free and internal rotations of the AC and reagents.

Analysis of the temperature dependence of the rate constant k using Eq. (14) is complemented by Eq. (15a)–(15c), where k_{max} is the

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[1] In the Marcus model [2,3] E_a^{eq} corresponds to the "working member" w_r, whereas E_a^{neq} corresponds to the free activation energy in the collision complex, ΔG^*.