

The role of intramolecular energy flow in surface unimolecular reactions

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Abstract

Two models of surface unimolecular reaction are considered: 1) the model with a rapid redistribution of adsorption energy within the degrees of freedom of the adsorbed molecule as well as of the solid phase, and 2) the model with a blocked energy flow into the solid phase. It is shown that lowering of the apparent activation energy of the reaction by blocking the energy flow into the solid phase could be observed for small and moderate molecules with sufficiently large adsorption energy.

Keywords: Energy flow; Surface reactions; Unimolecular reactions

1. Introduction

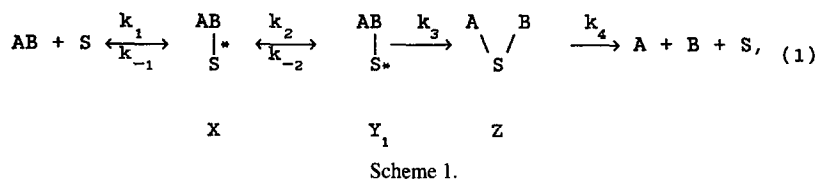
In the process of chemisorption, the new, adsorbed molecule–adsorption site bond is formed and the adsorption energy is released. It is plausible that this energy is, immediately after the adsorption, accumulated in the newly formed bond. In the classical texts on the theory of adsorption and surface reaction [1,2], it is tacitly assumed that the adsorption energy is rapidly randomized in the whole system, i.e. it freely flows into the adsorbed molecule as well as into the bulk of the solid phase. According to this idea, the adsorbed molecule and the solid phase have the same internal (vibrational) temperature. Recently, we postulated that the adsorption site blocks, in some cases (adsorption on heavy metals), the energy flow into the solid phase and the adsorption energy is randomized in the adsorbed

molecule only [3]. This postulate is based on the results of experiments and theoretical calculations suggesting that the heavy atom represents a serious barrier to the intramolecular energy flow in chemically activated molecules [4–8] and it is also supported by the interpretation of the width of fundamental and first overtone spectral lines of the acetylenic C–H stretch in $(\text{CH}_3)_3\text{CC}=\text{CH}$ and $(\text{CH}_3)_3\text{SiC}=\text{CH}$ molecules [9]. In this paper we discuss the measurable consequences of the blocking of free intramolecular energy flow into the solid phase by the adsorption site.

2. Model of surface unimolecular reaction

We shall consider a unimolecular decomposition of a molecule AB to products A and B on a catalyst with active sites S. In the first step, the molecule AB is adsorbed on an active site S and the adsorption energy is released. Then the

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adsorbed molecule decomposes to the adsorbed products A and B and these desorb into the gaseous phase. The reaction occurs when the energy greater than the threshold energy ϵ_0 accumulates in the critical bond (oscillator) A–B of the adsorbed molecule AB. The fate of the adsorption energy is the key point in following considerations.

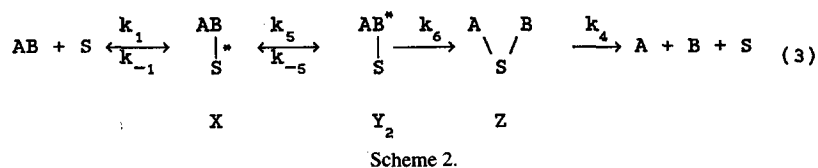
In the first limit case, the adsorption energy is transferred through the adsorption site S mostly into the bulk of the solid phase, and it is rapidly randomized there. The activation energy for a catalyzed reaction is then provided by the lattice vibrational modes of the catalyst and 'energy transfer takes place through surface atoms to the adsorbed entities that are prepared to react: each surface atom is more or less efficient channel through which vibrational quanta can pass' [10]. The corresponding reaction scheme is Eq. 1 (Scheme 1) in which * indicates the localization of adsorption energy, Y_1 is the surface complex with the adsorption energy randomized in the solid phase, k_1 and k_{-1} are the adsorption and desorption rate constants, respectively, k_2 is the rate constant of the energy flow from the intermediate X into the solid phase, k_{-2} is the rate constant of the energy flow from the solid state into the bond AB–S and k_4 is the rate constant of the desorption of products A and B. The probability of accumulation of energy greater than the threshold dissociation energy, ϵ_0 , in the critical bond A–B is equal to the equilibrium probability, $\exp(-\epsilon_0/k_B T_s)$, where T_s is the temperature of the solid phase (the solid phase represents a large heat bath which is in the continuous contact with the critical oscil-

lator). The rate constant k_3 is therefore given by the formula

$$k_3 = \omega \cdot \exp(-\epsilon_0/k_B T_s) \quad (2)$$

where the value of the preexponential term ω is the frequency of intramolecular energy redistributions and it is usually assumed of the order of 10^{13} s^{-1} .

In the second limit case, the adsorption energy is not transferred via the active site into the solid phase and the mechanism of a catalytic decomposition can be described by Eq. 3 (Scheme 2) [3]. (The generalized model of a molecule with oscillators divided into sets, where a rapid energy exchange exists within these sets, although between the separate sets there is no such exchange, was proposed already in the sixties [11]). In Eq. 3 (Scheme 2), * indicates the localization of adsorption energy, k_1 and k_{-1} are the adsorption and desorption rate constants of the molecules AB and the adsorbed molecules AB^*-S , respectively, k_5 is the rate constant of the energy transfer from the bond AB^*-S into the adsorbed molecule AB and k_{-5} is the rate constant of the energy flow from the adsorbed molecule AB^* into the bond AB–S. Further, k_6 is the rate constant of the breaking of the A–B bond in the adsorbed molecule AB^* and k_4 is the desorption rate constant of the products A and B. Applying the concepts of the RRK theory of unimolecular decomposition [12,13], the formula for the rate constant, k_6 , of the decomposition of the adsorbed molecules was derived [3]:



$$k_6 = \nu \cdot \int_{\epsilon_{\min}}^{\infty} [(\epsilon_a + \epsilon' - \epsilon_0) / (\epsilon_a + \epsilon')]^{s-1} (\epsilon' / k_B T)^{s-1} \cdot \exp(-\epsilon' / k_B T) d\epsilon' / \Gamma(s) k_B T \quad (4)$$

In Eq. (4), ν is the frequency constant of the order of 10^{13} s^{-1} , $\epsilon_{\min} = 0$ for $\epsilon_a > \epsilon_0$ and $\epsilon_{\min} = \epsilon_0 - \epsilon_a$ for $\epsilon_a < \epsilon_0$, ϵ_0 is the threshold (dissociation) energy of the A–B bond, ϵ' is the vibrational energy of the molecule AB in the gas phase, ϵ_a the adsorption energy ($\epsilon_a = q_a/N$, where q_a is the heat of adsorption in J/mol and N is the Avogadro number), s the number of representative oscillators of the adsorbed molecule AB, k_B the Boltzmann constant and T the temperature of the molecules AB in the gas.

The function $(\epsilon' / k_B T)^{s-1} \exp(-\epsilon' / k_B T)$ has the maximum at the point $\epsilon'_{\max} = (s-1)k_B T$. Substituting this value for ϵ' in the term $[(\epsilon_a + \epsilon' - \epsilon_0) / (\epsilon_a + \epsilon')]^{s-1}$ we obtain (for $\epsilon_0 < \epsilon_a + (s-1)k_B T$)

$$k_6 = \nu \cdot [1 - \epsilon_0 / (\epsilon_a + (s-1)k_B T)]^{s-1} \approx \nu \cdot \exp[-\epsilon_0 / (k_B T + \epsilon_a / (s-1))] \quad (5)$$

3. Overall rate constant and the apparent activation energy

The overall rate constant of the catalyzed decomposition $AB \rightarrow A + B$ for the first model is

$$r = -dN_{AB}/Sdt = k_3 L(Y_1) = k_3 L \Theta(Y_1) \quad (6)$$

where N_{AB} denotes the number of the molecules AB in the gas phase, S is the total surface of the catalyst and $\Theta(Y_1)$ is the surface coverage by the intermediate Y_1 ($\Theta(Y_1) = L(Y_1)/L$, where L is the total number of active centers per surface unit and $L(Y_1)$ is the number of centers occupied by the intermediate Y_1 per surface unit). Assuming the Langmuir type of adsorption–desorption equilibria and neglecting the surface coverage by products, $\Theta(Z)$, we can derive the rate equation

$$r = k_3 K_1 K_2 L N_{AB} / [1 + K_1 N_{AB} (1 + K_2)] \quad (7)$$

where $K_i = k_i/k_{-i}$. The low pressure limit ($N_{AB} \rightarrow 0$) of Eq. (7) is

$$r = k_3 K_1 K_2 L N_{AB} = k N_{AB} \quad (8)$$

where k is the low pressure limit of the overall rate constant. The constant k_3 is given by Eq. (2), the product $K_1 K_2$ is const. $\exp(\epsilon_a/k_B T)$. Therefore the apparent activation energy is

$$r = -k_B d \ln k / d(1/T) = \epsilon_0 - \epsilon_a \quad (9)$$

and it is independent of the temperature T .

The overall rate constant of the catalyzed reaction $AB \rightarrow A + B$ for the second model is

$$r = -dN_{AB}/Sdt = k_6 L(Y_2) = k_6 L \Theta(Y_2) \quad (10)$$

Assuming the Langmuir type of adsorption–desorption equilibria and neglecting the surface coverage by products we can derive the rate equation in the form

$$r = k_6 K_1 K_5 L N_{AB} / [1 + K_1 N_{AB} (1 + K_5)] \quad (11)$$

The low pressure limit of this equation is

$$r = k_6 K_1 K_5 L N_{AB} = k' N_{AB} \quad (12)$$

The constant k_6 is given by Eq. (5), the product $K_1 K_5$ is approximately equal to const. $(1 + \epsilon_a / sk_B T)^s$ (in the classical approximation $k_5 = \omega \cdot [1 - ((\epsilon - \epsilon_a) / \epsilon)^s]$ and $k_{-5} = \omega [(\epsilon - \epsilon_a) / \epsilon]^s$, where $\epsilon \approx sk_B T + \epsilon_a$). Therefore the apparent activation energy is (for moderate values of s)

$$\begin{aligned} \epsilon'_{\text{app}} &= -k_B d \ln k' / d(1/T) \\ &= \epsilon_0 / [\epsilon_a / (s-1)k_B T + 1] \\ &\quad [(\epsilon_a - \epsilon_0) / (s-1)k_B T \\ &\quad + 1] - \epsilon_a / (1 + \epsilon_a / sk_B T) \end{aligned} \quad (13)$$

and it generally depends on the temperature T . For very large s the apparent activation energy naturally limits to $\epsilon_0 - \epsilon_a$. The low temperature limit of ϵ'_{app} is equal to zero. The high temperature limit is $\epsilon'_{\text{app}} \rightarrow \epsilon_0 - \epsilon_a$. The lowering of the apparent activation energy by blocking the energy flow into the solid phase could therefore be observed at low pressures and low temperatures for small and

moderate molecules with sufficiently large adsorption energy. Let us note that the preexponential factor of the constants k' and k is ν and ω , respectively and it is in both cases of the order of 10^{13} s^{-1} .

Acknowledgements

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