Catalysis Letters 18 (1993) 177–182

# RRK model of unimolecular surface reaction

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Received 19 October 1992; accepted 8 December 1992

After the chemisorption of a polyatomic molecule on an active site of a catalyst, the adsorption energy is localized in the new, molecule-active site bond. Assuming the free flow of adsorption energy into the internal vibrations of the adsorbed molecules only, the Rice–Ramsperger–Kassel (RRK) statistical theory of a spontaneous decomposition can describe the surface reaction of these molecules. The mean vibrational energy of adsorbed molecules is determined by the temperature of reactants in the gas phase, and by the heat of adsorption.

**Keywords:** Intramolecular energy flow; surface reaction; RRK model

## 1. Introduction

The unimolecular catalytic decomposition and the bimolecular reaction of adsorbed molecules (either both adsorbed or one adsorbed and one from the gas phase) represent the basic types of surface reactions. The theory of these processes is based on an assumption of adsorption equilibria between gaseous reactants and adsorbed molecules obeying the Langmuir adsorption isotherm. Usually, the theory of absolute reaction rates is applied in the description of surface reactions [1,2]. We suggest that in the case of unimolecular surface reactions, the rate can be described using the concepts of the statistical (RRK) theory [3–5] of unimolecular reactions.

As an example, let us consider the decomposition $AB \rightarrow A + B$ occurring on active sites S on the surface of a catalyst. The reaction scheme of the reaction can be described by

$$AB + S \underset{k_d}{\overset{k_a}{\longleftrightarrow}} AB \cdot S\,, \tag{1}$$

$$AB \cdot S \xrightarrow{k_r} A + B + S\,, \tag{2}$$

where $AB \cdot S$ is the molecule AB adsorbed on a site S, $k_a$ and $k_d$ are the adsorption and desorption rate constants and $k_r$ is the rate constant of unimolecular surface reaction. According to this scheme, the adsorbed molecule AB decomposes and fragments of its decomposition desorb. Let us suppose that the unimolecular surface reaction is the rate controlling step. The concentration of AB · S is determined by the equilibrium of reaction (1). If both the adsorption and the desorption obey the Langmuir model the concentration, $n_{\mathrm{AB \cdot S}}$, of adsorbed molecules on the surface equals

$$n_{\mathrm{AB \cdot S}} = N\theta_{\mathrm{AB}}\,, \tag{3}$$

where $N$ is the total number of active sites (both occupied and free) on a unit surface area and the degree of coverage, $\theta_{\mathrm{AB}}$, is given by

$$\theta_{\mathrm{AB}} = \frac{k_{\mathrm{a}} p_{\mathrm{AB}}}{k_{\mathrm{a}} p_{\mathrm{AB}} + k_{\mathrm{d}}}\,, \tag{4}$$

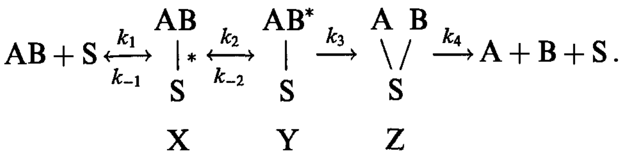
where $p_{\mathrm{AB}}$ is the partial pressure of molecules AB in the gas phase. The reaction rate on a unit surface area is given by

$$-\frac{\mathrm{d}n_{\mathrm{AB}}}{S\,\mathrm{d}t} = \frac{k_{\mathrm{a}} k_{\mathrm{r}} p_{\mathrm{AB}}}{k_{\mathrm{a}} p_{\mathrm{AB}} + k_{\mathrm{d}}}\,, \tag{5}$$

where $S$ is the total surface area of the catalyst.

## 2. The mechanism of the surface reaction

The fate of the adsorption energy (heat) after the adsorption is the key point in this consideration. If the adsorption energy is not transferred via the active site into the solid phase the mechanism of a catalytic decomposition can be represented by the following scheme:



$$\mathrm{AB}+\mathrm{S} \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} \begin{matrix}\mathrm{AB}\\ |*\\ \mathrm{S}\\ \mathrm{X}\end{matrix} \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} \begin{matrix}\mathrm{AB}^*\\ |\\ \mathrm{S}\\ \mathrm{Y}\end{matrix} \xrightarrow{k_3} \begin{matrix}\mathrm{A\ \ B}\\ \backslash /\\ \mathrm{S}\\ \mathrm{Z}\end{matrix} \xrightarrow{k_4} \mathrm{A}+\mathrm{B}+\mathrm{S}\,. \tag{6}$$

Here the symbols X, Y, and Z denote the surface intermediates, $*$ indicates the localization of adsorption energy, $k_1$ and $k_{-1}$ are the adsorption and desorption rate constants of the molecule AB and adsorbed molecule $\mathrm{AB}\overset{*}{-}\mathrm{S}$, respectively, $k_2$ is the rate constant of the energy transfer from the bond $\mathrm{AB}\overset{*}{-}\mathrm{S}$ into the adsorbed molecule AB and $k_{-2}$ is the rate constant of the energy flow from the adsorbed AB* molecule into the bond AB–S (the process $\mathrm{Y} \rightarrow \mathrm{X} \rightarrow \mathrm{AB} + \mathrm{S}$ represents a vibrationally induced desorption [6]). Further, $k_3$ 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 products. The surface is covered by the intermediates X, Y and Z. Let us assume that the reaction Y → Z, i.e. the breaking of the bond in the adsorbed molecule AB*, is the rate controlling step. Let $\theta_X$ and $\theta_Y$ denote the degrees of surface coverages by the intermediates X and Y. If the coverage by Z is neglected the total coverage equals $\theta_X + \theta_Y$. Further, we suppose that the adsorption of AB from the gas phase and the desorption from the "hot" bond containing $AB^{\ddagger}S$ are in the state of equilibrium,

$$\theta_X/(1 - \theta_X - \theta_Y) = k_1 p_{AB}/k_{-1} \tag{7}$$

and the coverage by the intermediate Y equals a stationary coverage which follows from reactions 2 and 3 in scheme (6):

$$\theta_Y = k_2\theta_X/(k_3 + k_{-2}) \,. \tag{8}$$

Eqs. (7) and (8) can be solved and the coverages expressed,

$$\theta_X = K_1 p_{AB}/[1 + K_1 p_{AB}(\alpha + 1)] \,, \tag{9}$$

$$\theta_Y = \alpha K_1 p_{AB}/[1 + K_1 p_{AB}(\alpha + 1)] \,, \tag{10}$$

$$\theta_X + \theta_Y = K_1 p_{AB}(\alpha + 1)/[1 + K_1 p_{AB}(\alpha + 1)] \,, \tag{11}$$

where $\alpha = k_2/(k_{-2} + k_3)$. For $k_3 \ll k_{-2}$, eq. (11) turns into the simple Langmuir isotherm with the equilibrium constant $K = K_1 K_2$ (where $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$). However, also the form of eq. (11) is similar to that of the Langmuir isotherm. The fraction $\theta_Y/\theta_X$ equals $\alpha = K_2/(1 + k_3/k_{-2})$. The resulting reaction rate is controlled by the reaction of the intermediate Y,

$$r = k_3\theta_Y = k_3\alpha K_1 p_{AB}/[1 + K_1 p_{AB}(\alpha + 1)] \,. \tag{12}$$

Now the RRK theory of unimolecular decomposition [3–5] can be applied for the evaluation of the rate constant, $k_3$, of the surface reaction Y → Z. The internal vibrational energy, $\epsilon$, of the molecule AB in the intermediate Y equals the sum of two components, $\epsilon = \epsilon_a + \epsilon'$, where the adsorption energy $\epsilon_a = q_2/N$, while $q_2$ is the heat of adsorption (J/mol) and $N$ is the Avogadro number, and the energy $\epsilon'$ is the vibrational energy of the molecule in the gas phase before the adsorption. We assume a rapid (on the picoseconds time scale) randomization of the internal vibrational energy over all vibrational degrees of freedom of the adsorbed molecule AB. The rate constant, $k_3$, corresponding to the breaking of the bond A–B in the adsorbed molecule, follows from the RRK formula:

$$k_3 = A\int_{\epsilon_{\min}}^{\infty}[(\epsilon_a + \epsilon' - \epsilon_0)/(\epsilon_a + \epsilon')]^{s-1} f(\epsilon')\,d\epsilon' \,, \tag{13}$$

where $\epsilon_0$ is the threshold energy necessary for the internal conversion (dissociation) of the adsorbed molecule AB (in general, it is not identical with the threshold energy of decomposition of the molecule in the gaseous phase) and the term

$[(\epsilon_a + \epsilon' - \epsilon_0)/(\epsilon_a + \epsilon')]^{s-1}$ is the probability that in the system of $s$ oscillators (vibrational modes of the molecule AB) with the total energy $\epsilon_a + \epsilon'$ an energy greater than $\epsilon_0$ will be concentrated in a particular (critical) oscillator. Further, $\epsilon_{\min} = 0$ for $\epsilon_a > \epsilon_0$ and $\epsilon_{\min} = \epsilon_0 - \epsilon_a$ for $\epsilon_a < \epsilon_0$. The product $f(\epsilon')\,d\epsilon'$ represents the probability, that the total vibrational energy of the molecule AB in the gas phase is $\epsilon'$ to $\epsilon' + d\epsilon'$ : $f(\epsilon') = (\epsilon'/k_BT)^{s-1} \exp(-\epsilon'/k_BT)/\Gamma(s)k_BT$ ($k_B$ is the Boltzmann constant and $\Gamma(s)$ is the gamma function). The adsorption energy $\epsilon_a$ and the sticking probability are considered independent of internal energy, $\epsilon'$, of the molecule AB before the adsorption. Therefore, the density $f(\epsilon')$ is at the same time the density of adsorbed molecules with the internal energy $\epsilon_a + \epsilon'$. The constant $A$ is the preexponential term of the RRK high-pressure rate constant and its value is of the order of $10^{13}$ s$^{-1}$. After substitution for $f(\epsilon')$ we obtain the expression for the rate constant of the surface reaction:

$$k_3 = A \int_{\epsilon_{\min}}^{\infty} [(\epsilon_a + \epsilon' - \epsilon_0)/(\epsilon_a + \epsilon')]^{s-1} (\epsilon'/k_BT)^{s-1} \times \exp(-\epsilon'/k_BT)/\Gamma(s)k_BT \tag{14}$$

with the limits $k_3 \to A \exp(-\epsilon_0/k_BT)$ for $\epsilon_a \to 0$ and $k_3 \to A$ for $\epsilon_a \to \infty$.

Assuming $\epsilon_a > \epsilon_0$ and large values of $s$, the expression for $k_3$ can be written in approximation (taking the value of the term $[(\epsilon_a + \epsilon' - \epsilon_0)/(\epsilon_a + \epsilon')]^{s-1}$ at the maximum of the function $(\epsilon'/k_BT)^{s-1} \exp(-\epsilon'/k_BT)$, i.e. at $\epsilon_{\max} = (s-1)k_BT$, and approximating this value by an exponential term) in the form

$$k_3 = A \exp\left(-\frac{\epsilon_0}{\epsilon_a/(s-1) + k_BT}\right). \tag{15}$$

According to eq. (15), the apparent activation energy, $\epsilon_{\text{app}}$, of the surface reaction increases with increasing temperature of the gas: $\epsilon_{\text{app}} = -k_B[d \ln k_3/d(1/T)] = \epsilon_0/[\epsilon_a/(s-1)k_BT + 1]^2$. The mean vibrational energy of molecules AB in the gas phase is $sk_BT$ and in the intermediate Y it is $sk_BT + \epsilon_a$; the latter value corresponds to the apparent vibrational temperature $T' = T + \epsilon_a/sk_B$ (according to eq. (15), the apparent temperature is $T + \epsilon_a/(s-1)k_B \approx T'$).

The value of the order of $10^{12}$ s$^{-1}$ should be expected for the constant $k_2$ because the flow of energy from the excited bond to the rest of the molecule is accomplished on the picosecond time scale [7–10]. The value of the constant $k_{-2}$ may be estimated on the basis of the following considerations: The system AB–S can be represented by $s$ oscillators of AB and one oscillator corresponding to the bond AB–S, i.e. by $s + 1$ oscillators. The ratio of the number of surface molecules AB– S having an energy greater than $\epsilon_a$ localized in the bond AB–S to the number of AB–S having that energy lower than $\epsilon_a$ is approximately equal to $[\epsilon'/(\epsilon' + \epsilon_a)]^s$. Therefore, $\theta_X/\theta_Y \approx k_{-2}/k_2 \approx [\epsilon'/(\epsilon' + \epsilon_a)]^s$ and $k_{-2} \approx k_2[\epsilon'/(\epsilon' + \epsilon_a)]^s$. We can expect $\alpha \gg 1$ in eqs. (9)–(11).

In preceding considerations, the energy flow across the bond AB–S into the solid phase (into the nearest neighborhood of the active site S) was neglected. This simplification is justified to some extent in the case of adsorption on heavy metals, as a heavy atom blocks the intramolecular transfer on vibrational energy [11–14]. The adsorption site is therefore considered an immobile structureless point and the temperature of the solid phase is of no importance. The mean energy of the system AB–S is determined by the temperature of gas phase and by the adsorption energy only. If we abandon this concept and permit the rapid energy flow via the active site to and from the solid phase, the latter acts as a large heat bath (thermostat) of temperature $T$, and the system AB–S reaches the thermal equilibrium with it. At equilibrium the probability of accumulation of energy $\epsilon$ to $\epsilon + \mathrm{d}\epsilon$ in the critical bond of adsorbed molecule AB is equal to $\exp(-\epsilon/k_\mathrm{B}T)\,\mathrm{d}\epsilon/k_\mathrm{B}T$. The probability that there is accumulated an energy greater than $\epsilon_0$ is then $\int_{\epsilon_0}^{\infty} \exp(-\epsilon/k_\mathrm{B}T)\,\mathrm{d}\epsilon/k_\mathrm{B}T = \exp(-\epsilon_0/k_\mathrm{B}T)$. The rate constant of the surface reaction is proportional to the latter probability,

$$k_3 = \nu \exp(-\epsilon_0/k_\mathrm{B}T)\,. \tag{16}$$

The temperature $T$ in eq. (16) is the temperature of the thermostat, i.e. the temperature of the solid phase. The activation energy $-k_\mathrm{B}[\mathrm{d}\ln k_3/\mathrm{d}(1/T)] = \epsilon_0$ is independent of the temperature $T$. This model is an equilibrium one, and it does not enable any closer interpretation of the constant $\nu$. However, it can plausibly be assumed that the molecules with an energy greater than the threshold energy in the critical oscillator decompose with the rate constant of the order of the vibrational frequency of the critical bond, i.e. $\nu \approx 10^{13}\ \mathrm{s}^{-1}$. The theory of absolute reaction rates offers for the rate constant of a unimolecular surface reaction a formula identical with eq. (16) in which $\nu = k_\mathrm{B}T/h$ ($h$ is the Planck constant), provided that the partition function of the activated complex is approximately the same as the partition function of the adsorbed molecule [1,2].

## Acknowledgement

The support of the Czechoslovak Academy of Sciences (Grant No. 43212) is gratefully acknowledged.

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