On the Changes of Rate Constants and Activation Energies during Catalytic Reactions. Decomposition of NaOCl and H_2O_2

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Summary. It has been observed that catalytic reactions can proceed according to several rate constants and *Arrhenius* activation energies. Changes of rate constants occurs periodically with increasing numbers of moles of substrate, especially when the number of moles of substrate at the initial state is high compared with the amount of catalyst. It has been suggested that the difference in the mole number between two consecutive changes of a rate constant can be used as a measure of the effective catalyst concentration in homogeneous systems or of the number of active sites on the surface of a catalyst in heterogeneous systems.

Keywords. Catalysis; Rate constant; Activation energy; Active sites.

Zu den Änderungen von Geschwindigkeitskonstante und Aktivierungsenergie bei katalytischen Reaktionen. Zersetzung von NaOCl und H_2O_2

Zusammenfassung. Es wurde gefunden, daß katalytische Reaktionen mit verschiedenen Geschwindigkeitskonstanten und Aktivierungsenergien verlaufen können. Der Wechsel der Geschwindigkeitskonstante tritt periodisch bei bestimmten Substratmengen auf, besonders wenn zu Beginn der Reaktion die Substratmenge gegenüber der Katalysatormenge hoch ist. Der Unterschied in der Molzahl zwischen aufeinanderfolgenden Änderungen der Geschwindigkeitskonstante wurde als Maß für die effektive Katalysatorkonzentration (in homogenen Systemen) oder für die Zahl der aktiven Zentren an der Katalysatoroberfläche (in heterogenen Systemen) vorgeschlagen.

Introduction

Recently, *Larsson* has shown that the experimentally determined *Arrehenius* activation energy (E_a) is a multiple of a constant value of energy (ΔE) equal to 1–2 kcal/mol [1–3]. He suggests that the activation energy changes stepwise by constant values of ΔE. As a consequence, the rate constant should, also change stepwise. In 1989, the same phenomenon has been observed with the decomposition of hydrogen peroxide in the presence of iron polyphthalocyanine as a heterogeneous catalyst [4].

As has been shown the free enthalpy of active complexe formation is the sum of the reaction enthalpy and of a contribution from the activation entropy of an active complex [5]. The enthalpy of active complex formation has a constant value under

defined experimental conditions. However, the value of entropy depends on its environment and concentration. The aim of this work is to show – on the basis of sodium hypochlorite [6] and hydrogen peroxide decomposition – that catalytic reactions can proceed according to several rate constants and that the stepwise character of the catalysis is caused by the periodical action of the active sites under the initial conditions when the number moles of substrate is high compared to the amount of catalyst.

Results and Discussion

Figure 1 presents the dependence of the logarithm of the initial substrate mole number (n) upon time for the decomposition of sodium hypochlorite for different values of n and constant catalyst mass.

It can be seen from Fig. 1 that the reaction proceeds as 1st order reaction [7] at different rate constants depending on n: The higher the initial number of moles of a substrate, the greater the number of rate constants. The change of rate constant occurs at constant intervals Δn. At the final range of Δn the rate constant reaches a maximum value, but the turnover frequency in the consecutive ranges of Δn decreases, indicating that the catalytic activity decreases during the reaction.

The main characteristic feature of this reaction is that the differences of substrate mole numbers (marked in Fig. 1 and 2 as Δn) corresponding to two consecutive
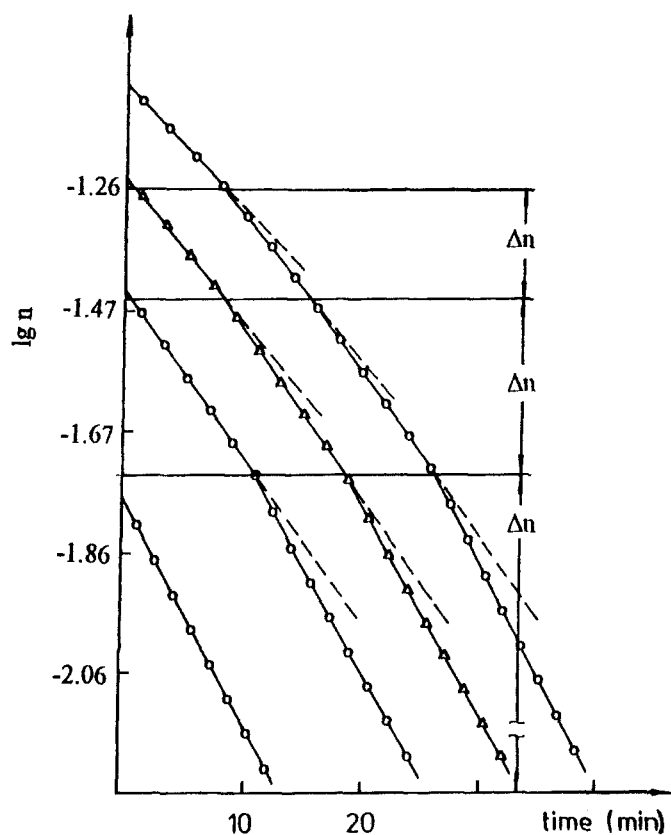
Fig. 1. Dependence of $\lg n$ upon time for sodium hypochlorite decomposition with different initial concentrations; $pH = 11.8$, $T = 333$ K
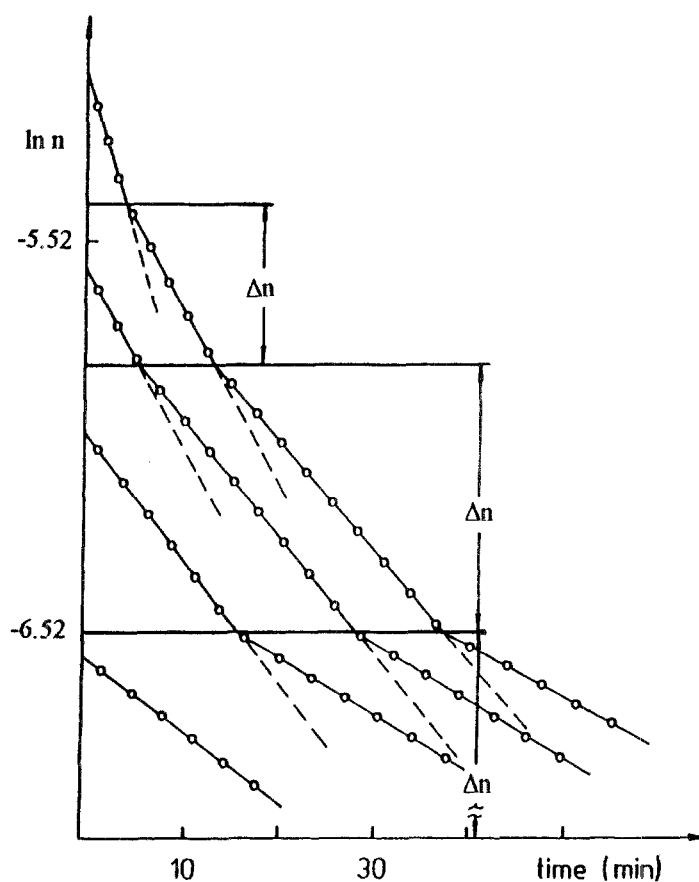
Fig. 2. Dependence of $\ln n$ upon time for hydrogen peroxide decomposition with different initial concentrations; $T = 323$ K

changes of rate constants are constant for given catalyst mass and independent of temperature.

Figure 2 presents the dependence of $\ln n$ vs. t for the decomposition of H_2O_2 in the presence of Pt. It follows from Fig. 2 that in this case the reaction also proceeds stepwise according to several rate constants with constant Δn for consecutive changes.

As can be seen from Figs. 1 and 2, the direction of changes of rate constants in both reaction is opposite. In the case of NaOCl decomposition, the consecutive rate constants increase, whereas in the reaction of H_2O_2 decomposition they decreases. This results from the change of entropy of active complexes formation.

From the dependence of $\ln k$ upon $1/T$, the activation energy in each range of Δn can be determined. The analysis of experimental data concerning the activation energy point out that the difference of activation energy corresponding to two consecutive changes of rate constant is constant within the bounds of experimental error. For the decomposition of NaOCl it amounts to 1.38 kcal/mole. For the initial period of NaOCl decomposition, the highest activation energy is observed (E_1); at the final stage, the activation energy is the lowest one (E_5).

Figure 3 presents the dependence of activation energy on Δn scale for NaOCl decomposition. The changes are in the line with the suggestion of *Larsson* and in the same range as those presented by him [1].
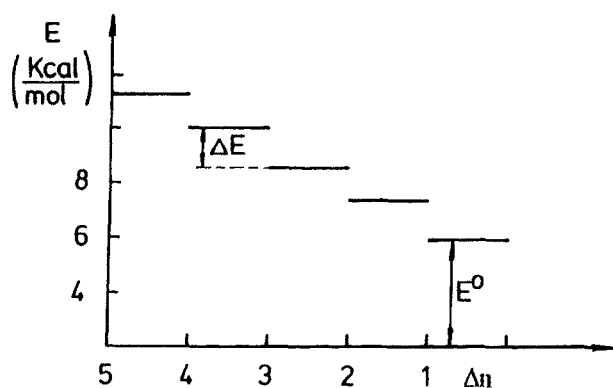
Fig. 3. Dependence of activation energy on the substrate concentration (expressed in Δn) for sodium hypochlorite decomposition
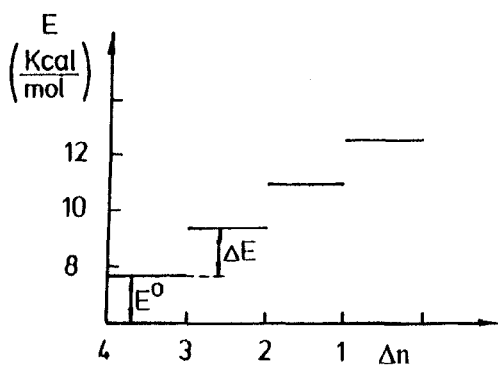

Fig. 4. Dependence of activation energy on the substrate concentration (expressed in Δn) for hydrogen peroxide decomposition

In the case of the decomposition of the H_2O_2 the direction of change of activation energy is opposite to that observed in the case of NaOCl decomposition. The differences of ΔE, however, are constant, too.

Figure 4 presents the dependence of activation energy on Δn for H_2O_2 decomposition. In this case, the lowest activation energy is observed within the first range of Δn, i.e. in the initial period of reaction.

In order to explain the course of reaction according to several rate constants, the catalytic reaction in the case of homogeneous systems can be described as

$$mA + K \leftrightarrow (AK)^* + (m-1)A \rightarrow (m-1)A + P + K \tag{1}$$
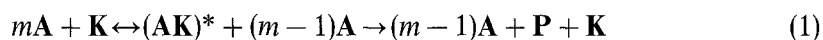
where A = substrate, K = catalyst, $(AK)^*$ = active complex, P = product, and m = current excess of moles of substrate regarding the number of moles of catalyst.

In a heterogeneous catalytic system, where N = Avogadro's constant, the reaction can be represented by Eq. (2):

$$m(\Delta n \cdot N)A + (N \cdot \Delta n)K \leftrightarrow (AK)^* + (m-1)(\Delta n \cdot N)A \rightarrow (m-1)(\Delta n \cdot N)A + P + K \tag{2}$$
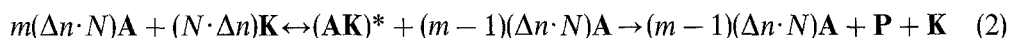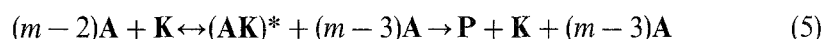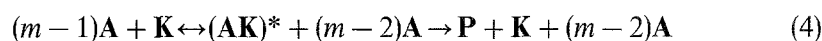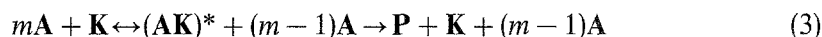
The product $N \cdot \Delta n$ determines the number of active sites on the surface of a catalyst used in the reaction.

In case of the reaction described in Eq. (1), the reaction from substrate to product proceeds by "portions" because the catalyst can be bound into the active complex only by the limited number of moles of substrate. A "portion" therefore determines

a quantity of substrate which can be bound stoichiometrically by the catalyst into the active complex. Since the change of a rate constant occurs periodically at every constant values of Δn, it can be assumed that the active complex is always created by the same quantity of Δn substrate moles and active sites. This points to α strong stoichiometry of the catalytic processes.

Assuming that the considered active complex arises from a substrate molecule and a catalyst active site in the ratio of 1:1, the consecutive reaction of "portions" on the way from substrate to a product according to Eq. (1) can be writen as follows:

$$mA + K \leftrightarrow (AK)^* + (m-1)A \rightarrow P + K + (m-1)A \tag{3}$$

$$(m-1)A + K \leftrightarrow (AK)^* + (m-2)A \rightarrow P + K + (m-2)A \tag{4}$$

$$(m-2)A + K \leftrightarrow (AK)^* + (m-3)A \rightarrow P + K + (m-3)A \tag{5}$$

$$\vdots$$

$$2A + K \leftrightarrow (AK)^* + A \rightarrow P + K + A \tag{6}$$

$$A + K \leftrightarrow (AK)^* \rightarrow P + K \tag{7}$$

From a statistic thermodynamics point of view, reactions (3)–(7) proceed under different conditions of thermodynamic probability. Therefore, consecutive active complexes are characterized by different values of activation entropy. The entropy of activation is determined by parameters which characterize structures of substrate molecules and activated complexes, *i.e.* by vibrational frequencies, interatomic distances, atomic masses *etc.* Taking into consideration the theory of absolute reaction rate in which the rate constant is described as

$$k = \frac{k_B T}{h} \exp(\Delta S^*/R)\exp(-\Delta H^*/RT), \tag{8}$$

it is evident that not only the enthalpy of an active complex but also its entropy decide about the value of the rate constant. This entropy depends on the structure of reacted molecules and that of the activated complex.

From Eq. (8), Eqs. (9a) and (9b) may be derived for m and $m-1$, respectively $\left(G = \frac{k_B T}{h}\right)$:

$$\ln k_m = \ln G + \Delta S_m^*/R - \Delta H^*/RT \tag{9a}$$

$$\ln k_{m-1} = \ln G + \Delta S_{m-1}^*/R - \Delta H^*/RT \tag{9b}$$

Substraction of Eq. (9a) from Eq. (9b) affords

$$\ln \frac{k_{m-1}}{k_m} = \frac{\Delta S_{m-1}^*}{R} - \frac{\Delta S_m^*}{R} \tag{10}$$

In the case of the decomposition of NaOCl it follows from the experimental data that

$$k_{m-1} > k_m \text{ and } \ln \frac{k_{m-1}}{k_m} > 0 \tag{11}$$

Therefore,

$$|\Delta S_{m-1}^*/R| > |\Delta S_m^*/R| \tag{12}$$

The last relation demonstrates that during the reaction the absolute value of entropy increases.

For the decomposition of H_2O_2 we have

$$|\Delta S^*_{m-1}/R| < |\Delta S^*_m/R|, \tag{13}$$

indicating that the absolute value of entropy decreases as the reaction proceeds.

The periodical changes of rate constants at every constant Δn suggests that the catalyst binds a number of moles of substrate equivalent to the number of active sites. For this reason, Δn can be a measure of effective catalyst concentration in the homogeneous system or a measure for the number of active sites on the catalyst surface in case of heterogeneous catalytic systems.

Other experimental data show that in homogeneous system in which the catalyst concentration is known Δn corresponds to the concentration of the catalyst [11]. This fact confirms well the suggestion mentioned above.

The above conclusion is going well with the observation that the value of Δn in the NaOCl as well as in the H_2O_2 decompositions depends linearly on the catalyst mass.

In Tables 1 and 2, the values of activation energy for the decomposition of NaOCl and H_2O_2, respectively, are given. According to these data and Figs. 3 and 4, we can write

$$E_{exp} = E^0 + a\Delta E \tag{14}$$

Table 1. NaOCl decomposition (303–333 K, $pH = 11.8$): activation energy differences for different ranges of concentration; $\Delta n = 0.018$; $\Delta E_{exp} = 1.38$ kcal/mol

	E_{exp} (kcal/mol)	ΔE_{exp} (kcal/mol)
$5\Delta n \rightarrow 4\Delta n$	11.64	
		1.45
$4\Delta n \rightarrow 3\Delta n$	10.19	
		1.36
$3\Delta n \rightarrow 2\Delta n$	8.83	
		1.31
$2\Delta n \rightarrow 1\Delta n$	7.52	
		1.43
$1\Delta n \rightarrow 0$	6.09	

Table 2. H_2O_2 decomposition (303–333 K): activation energy differences for different ranges of concentration; $\Delta n = 0.1$; $\Delta E_{exp} = 1.56$ kcal/mol

	E_{exp} (kcal/mol)	ΔE_{exp} (kcal/mol)
$4\Delta n \rightarrow 3\Delta n$	7.92	
		1.53
$3\Delta n \rightarrow 2\Delta n$	9.45	
		1.63
$2\Delta n \rightarrow 1\Delta n$	11.08	
		1.52
$1\Delta n \rightarrow 0$	12.60	

where E_{exp} = experimentally determined activation energy according to the *Arrhenius* equation, E^0 = indivisible part of activation energy, a = number of activation energy change, and ΔE = difference of activation energy between two consecutive values.

Experimental

The catalyst for the decomposition of H_2O_2 was obtained by impregnation of active carbon "Carbopol N" with chloroplatinic acid: 1 g of active carbon (880 m^2/g) was immersed in chloroplatinic acid to get 5% w/w surface concentration of Pt. After evaporation of water, Pt ions were reduced in a hydrogen atmosphere. Depending on the temperature of this process, the final platinum crystallites exhibit different sizes which were estimated applying the WAXS method by means of a DRON 1 apparatus using CuKα radiation [12]. Crystallite sizes were within the range of 8 to 30 nm.

The decomposition of sodium hypochlorite in the presence of Co_3O_4 as a catalyst was studied. The catalyst was obtained by impregnating a carrier (aluminum magnesium spinell) with a 2 M cobalt nitrate solution during 24 h, drying, and annealing at 480 K [7]. The covering by Co_3O_4 amounted to 4.5% w/w.

Catalytic activity

The decomposition of hydrogen peroxide was performed at concentrations ranging from 0.005 to 0.2 mol/dm^3 at 288 to 323 K. The concentration changes of H_2O_2 during the reaction were determined manganometrically. Within the whole range of H_2O_2 concentration, the reaction order was equal to 1 [8-10]. The decomposition of NaOCl was carried out at different initial concentrations and temperatures at pH = 11.8. Samples were taken at defined time intervals, and the content of active chlorine was determied iodometrically.

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