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On the Stepwise Change of Rate Constant and Activation Energy at the Catalytical Decomposition of NaClO

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Summary. It has been found that the catalytic decomposition of NaClO proceeds according to several rate constants and activation energies. The changes of rate constants and activation energies appear periodically at constant intervals of NaClO concenration.

Keywords. Catalyst concentration; Number of active sites; Stepwise change of activation anergy; Stepwise change of rate constant.

Zur stufenweisen Änderung von Geschwindigkeitskonstante und Aktivierungsenergie bei der katalytischen Zersetzung von NaClO

Zusammenfassung. Die katalytische Zersetzung von NaClO verläuft je nach Substratkonzentration mit verschiedener Geschwindigkeitskonstante und Aktivierungsenergie. Die Änderungen erfolgen periodisch; die Unterschiede in der Konzentration von NaClO zwischen zwei Stufen (Δc) sind jeweils konstant.

Introduction

By analysis of many experimental data concerning catalytical reactions, *Larsson* recently has shown that the experimentally determined activation energy always is a multiple of a constant value of energy [1–3]. He suggests that the activation energy changes stepwise by a constant value ΔE. If this suggestion holds true, the rate constants should also change stepwise.

In 1989, we described a catalytic reaction proceeding according to several rate constants (decomposition of hydrogen peroxide in the presence of iron polyphthalocyanine as catalyst [4]). The aim of this paper is to show that the catalyic decomposition of NaClO can proceed according to several rate constants when the substrate concentration is high compared to the catalyst mass.

Results and Discussion

Figure 1 shows the dependence of lg$c$ on time for the decomposition of NaClO for different initial concentrations at constant catalyst mass.

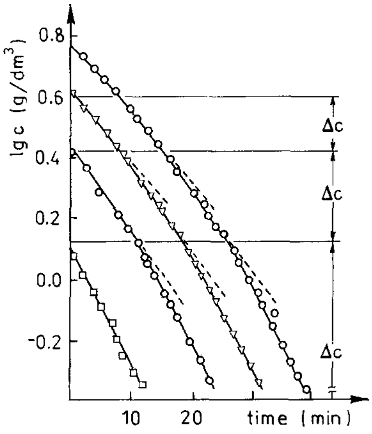

Fig. 1. Dependence of lg$c$ on time for the decomposition of NaClO for different initial concentrations; temperature: 323 K

It can be seen (Fig. 1) that the reaction proceeds stepwise as a 1st order reaction according to several rate constants. It is also obvious that the number of rate constants depends on the initial concentration of substrate (at constant catalyst mass). The greater the initial concentration of substrate, the greater is the number of rate constants.

The difference of substrate concentrations between two consecutive changes of rate constant (marked in Figs. 1 and 2 as Δc) is constant. This is a characteristic feature for the reaction presented here. Δc is independent of temperature within detection limits.

Since the reaction proceeds according to several rate constants, the dependence of ln$k$ on $1/T$ can be investigated for every range of Δc and for different temperatures. The activation energy in this range of Δc can then be determined. Such a procedure is shown in Figs. 2a and 2b. The analysis of the experimental data presented in Fig. 2 shows that the difference of energy between two consecutive changes of activation energy is constant within error limits and- in this case- is equal to 1.38 kcal/mole.

From the experimental data presented in Figs. 2a and 2b it results that the highest activation energy (E_1) is observed for the initial period of NaClO decomposition whereas in the final period of Δc the energy is lowest (E_5). The difference between the consecutive values is constant. From this observation it can

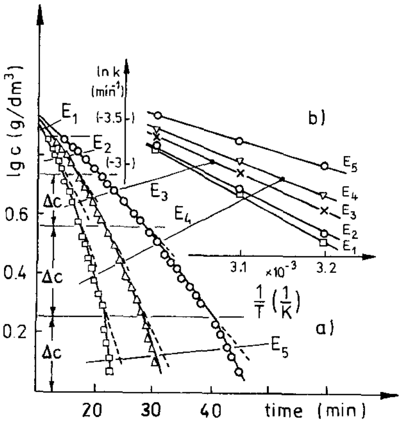

Fig. 2. Dependence of lg$c$ on time for different temperatures (a) and ln$k$ on reverse temperature for the decomposition of NaClO in different ranges of concentration (b)

be stated that the activation energy changes stepwise (analogous to the stepwise changes of rate constants) at constant values of energy. This is in accordance with the suggestion of Larsson [1].

Other experimental data [5] show that in the homogeneous system, in which the catalyst concentration is smaller than the substrate concentration, the value of Δc is equal to the concentration of homogeneous catalyst. This fact leads to the suggestion that the catalyst binds an equivalent amount of substrate. Therefore the value of Δc might serve as a measure of the effective catalyst concentration in homogeneous systems or of the number of active sites on the catalyst surface in the case of heterogeneous catalytic systems. However, this suggestion still lacks verification. The dependence of Δc on the catalyst mass has a linear character. This linearity is obviously due to the fact that the number of active sites is proportional to the surface area and the surface area is proportional to the catalyst mass.

A reaction proceeding according to several rate constants is possible when the substrate concentration is greater than the catalyst concentration (for homogeneous systems) or when the number of substrate molecules is greater than the number of active catalyst sites in the system (for heterogeneous systems). Possibly, such stepwise changes of rate constant and activation energy may occur for all homogeneous catalytical systems in which the substrate concentration is greater than the catalyst concentration.

Experimental

The catalyst was obtained by impregnation of a carrier with a solution of $Co(NO_3)_2$ ($2M$) during 24 h; then it was dried and annealed at 480 K. The amount of Co_3O_4 on the carrier (aluminum-magnesium spinel) was 4.5% (w/w). The decomposition of NaClO was carried out at different initial concentrations and different temperatures at $pH = 11.8$.

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