PSEUDODIFFUSION-CONTROLLED REACTIONS

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SUMMARY

A novel type of bimolecular liquid-phase reactions entitled "pseudodiffusion-controlled" is described. Rate of a pseudodiffusion reaction is inversely viscosity proportional as for a diffusion-controlled reaction but pseudodiffusion reaction proceeds slower than a diffusion-controlled one. The reason lies in steric constraints to pseudodiffusion reaction. A comparative analysis of diffusion-, activation-controlled, and pseudodiffusion reactions is given. Different boundary conditions for diffusion equations manifest themselves in different reaction types. Examples of pseudodiffusion-controlled reactions are presented.

INTRODUCTION

Any bimolecular reaction in solution proceeds in two stages, i.e. a diffusion of reagent molecules towards each other till a contact, and a chemical transformation of reagent pair to products. It is belived that reagents diffuse to a reaction radius ρ, close to a sum of van der Waals radii of reagents. So, we consider here contact reactions. In special cases such reactions as electron or energy transfer are not contact ones and occur at distances $r > \rho$.

A rate constant of the bimolecular reaction under stationary conditions is obviously a product of the diffusion rate constant and the probability of a chemical reaction or chemical act proper p:

$$k = k_{diff}\, p \qquad\qquad (1)$$

Depending on the p-value and its viscosity (η) dependence bimolecular reactions fall into three principally different classes.

DIFFUSION-CONTROLLED REACTIONS

The correct physical approach to a problem of bimolecular reaction is a solution of the diffusion equation, see for review /1-3/:

$$\partial C(r,t)/\partial t = \nabla^2 C(r,t) \qquad (2)$$

where C is a time and interparticle distance dependent concentration. The initial condition to eq. (2) is $C(r,0) = C_0$ and the boundary condition to the equation is the following:

$$4 \pi \rho^2 D \left(\frac{\partial C(r,t)}{\partial r} \right)_{r=\rho} = k_{act} \cdot C(\rho,t) \qquad (3)$$

where D is mutual diffusion coefficient and k_{act} [$M^{-1} s^{-1}$] may be considered as a second order rate constant of the cage reaction /1/.

Integration of eq. (3) over **r** leads to the equation:

$$C(\rho,t) = \frac{C(\infty, t)}{1 + k_{act}/4 \pi \rho D} \qquad (4)$$

The value of $C(\infty,t)$ is an experimentally measured concentration of a reagent.

The Smoluchowski (1917) boundary condition means the infinite rate of chemical act ($k_{act} \rightarrow \infty$) and $C(\rho, t) = 0$, and P=1. This situation — reagents react much faster than diffuse apart — corresponds to the **diffusion-controlled reaction**. The rate constant of a diffusion-controlled reaction is described by the well-known equation /1-3/:

$$k = k_{diff} = 4\Pi\rho D \qquad (5)$$

The reagents participating in diffusion-controlled reactions are sometimes termed "black spheres" /2, 3/, Fig. 1.

The k_{diff}-value is expected to be inversely η–dependent because $D \sim \eta^{-1}$ according to the Stokes-Einstein equation. Fig. 2 shows such a dependence. However, in practice one can obtain $k \sim \eta^{-\alpha}$, where $0.5 \leq \alpha \leq 1.2$ for a completely diffusion-controlled reaction /3/.
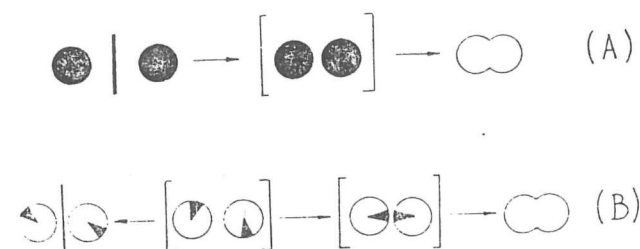
Fig. 1. A scheme of reaction between black spheres (A) and between white spheres with black spots (B). The square brackets indicate that the spheres are in the solvent cage.
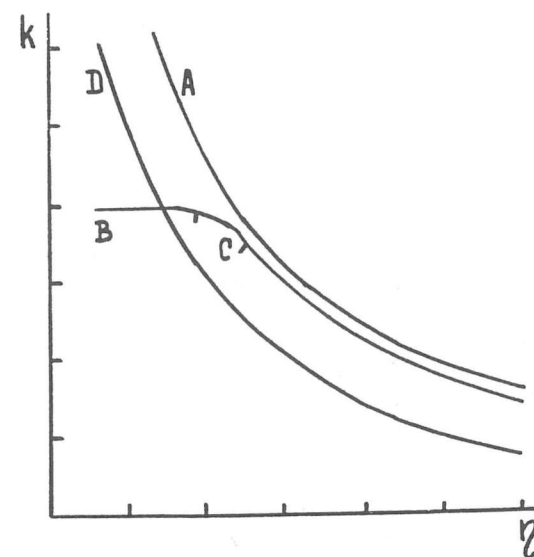

Fig. 2. Typical dependences of rate constant upon viscosity for the following reaction types:
(A) diffusion-controlled; (B) activation-controlled; (C) diffusion-enhanced; (D) pseudodiffusion-controlled.

DIFFUSION-ENHANCED AND ACTIVATION-CONTROLLED REACTIONS

The first term is used for a reaction whose rate weakly depends upon a diffusion rate of reagents. For a diffusion-enhanced reaction $0.1 \leq p < 1$. If the rate constant of a reaction is independent of η, the reaction is often termed **"activation-controlled"**. (This definition probably is not very good because in some special cases a diffusion independent reaction may have no activation energy or even negative E_{act}). Activation-controlled reactions have been studied in chemical kinetics over many decades.

Reagents participating in diffusion-enhanced and activation-controlled reactions may be called "grey spheres". The k_{act}-value for these reactions is a finite value and $C(\rho, t) > 0$, cf. eq. (3, 4).

The following equations hold true for the diffusion-enhanced or the activated reaction:

$$k = k_{diff} \cdot k_{act}/(k_{act} + k_{diff}) \tag{6a}$$

$$k^{-1} = k_{diff}^{-1} + k_{act}^{-1} \tag{6b}$$

If $k_{act} \ll k_{diff}$, a reaction is an activation-controlled one, if $k_{act} \gg k_{diff}$, a reaction is a diffusion-controlled one. If $k_{act} \approx k_{diff}$, a reaction is a diffusion-enhanced one.

An activation-controlled reaction will be a diffusion-enhanced or even a diffusion-controlled one in sufficiently viscous media (Fig. 2).

There is a number of problems related to the correct choice of boundary conditions related to a mode of molecules movement (continuous diffusion or jumps of arbitrary lengths). These problems have been discussed in ref. /5, 6/.

REACTIVITY ANISOTROPY

We have considered above reagents with isotropic reactivity. That means that molecules react with the same probability at any contact. However complicated molecules (free radicals) have a relatively small reaction site or reaction spot on their van der Waals surface. It is well known, for example, that enzymes have reaction sites.

The reaction spot may be extremely reactive, so that any contact of a reagent molecule with the spot will lead to a reaction. Such a reagent may be termed "white sphere with black spot". So, the reaction in a sense would be controlled by diffusion. But the diffusion has to lead not only to a contact of two molecules, but to the contact of proper parts of them. Certainly, the latter is a more severe requirement than just a contact, and the rate constant of such reaction will be less than k_{diff}.

The pertinent theoretical description becomes a complicated problem relating to a diffusion in multidimensional space including angular variable(s) of reagent(s). For review see /2/. The corresponding boundary condition in the case of one sphere with black spot is the following:

$C(\rho, t) = 0$ at $\emptyset \leq \emptyset_0$ (on the active surface)

$$\tag{7}$$

$\partial C(r, t)/\partial \varphi = 0$ at $\emptyset > \emptyset_0$ (on the inert surface region)

Here, polar angle $\emptyset_0$ gives the relative size of a spot, $0 < \emptyset < \Pi$, $\partial / \partial \varphi$ denotes the normal derivative.

The geometric steric factor f_g is equal to the statistical weight of orientations that are favorable for the reaction. In the liquid phase, owing to the cage effect the anisotropy of reactivity may be partially, or even wholly averaged (Fig. 2). If in their first contact the spheres with black spots have approached each other in an unfavorable orientation, they will have a chance to change their orientation before they meet again and react (Fig. 2).

Thus the cage effect rises f_g up to the effective steric factor f_{eff}. Diffusion-controlled reactions between highly reactive reagents, at least one of them is characterized by profound reactivity anysotropy, have been entitled **"pseudodiffusion-controlled reactions"**.

For a pseudodiffusion reaction the following holds true:

$$k = k_{diff} \cdot f_{eff} \tag{8}$$

So, diffusion-controlled reactions may be considered as a particular case of pseudodiffusion reactions ($f_{eff} = 1$), cf. eqs. (5, 8). Indeed, $f_{eff} = 1$ when $\emptyset_0 = \Pi$, or even $\emptyset_0 < \Pi$ but is relatively large value /2/.

Fig. 2 presents a typical dependence of k vs. η for a pseudodiffusion reaction, and Fig. 3 presents a concrete example of such a plot.
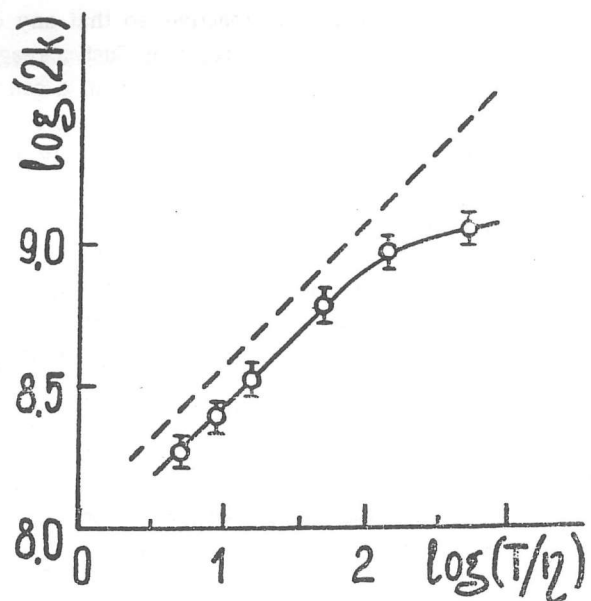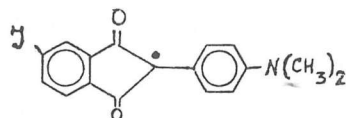
Fig. 3. Dependence of C-centered radical recombination rate on viscosity of the toluene/vaseline oil binary mixture T = 298 K, η is in cPs. The dotted line is the dependence of k_{diff} on η.

The radical has a structure of

One can see that the reaction spot, i.e. the central trivalent carbon atom's surface, is rather small compared with the all radical's surface /7/.

CONCLUSIONS

When an experimentalist measures a rate constant of fast bimolecular reaction $k \approx 10^5$ - 10^{10} M^{-1}. s^{-1} the question immediately arises: Is a reaction diffusion - or activation-controlled? Obviously it is necessary to know the reaction type in order to find ways to govern a reaction. The question may be stated in a form: what does rate constant and other kinetic parameter reflect: the rate of <u>chemical</u> transformation of reagents into products, or a rate of <u>physical</u> process, i.e. a rate of mutual diffusion?

A viscosity dependence of rate constant helps one to obtain an answer to the question stated above. One must be careful not to confuse an activation- with a pseudodiffusion-controlled reaction on the basis of the inequality $k < k_{diff}$ alone. All of the experimental criteria for establishing the reaction type are presented in ref. /3/.

A steric factor in bimolecular reactions has been widely discussed in chemical kinetics. In the collision theory a steric factor is a coefficient at the number of double collisions $Z \approx 10^{11}$ M^{-1} . s^{-1}. According to the collision theory:

$$k = k_{act} = p . Z . e^{-E_{act}/RT} \qquad (9)$$

It seems doubtful to find a direct relationship between f_g and p. These steric factors may be proportional each other within a certain reaction series. As was mentioned above, f_g has a purely geometrical nature, whereas p is related to the ratio of partition functions /8/.

It is trivial to say at present that energy and entropy govern rates and equilibria of chemical reactions. An increase of steric hindrances around a reaction center leads in most cases to deceleration of a bimolecular reaction due to both activation entropy decrease and activation energy increase. In a majority of cases there is a compensation between $\log(pZ)$ and E_{act} or between $\Delta S^{\neq}$ and $\Delta H^{\neq}$ within a reaction series. However, in the case of diffusion-controlled reaction an increase of steric constraints to a reaction manifests itself only in geometrical limitations to a reaction and leads only to $\Delta S^{\neq}$ decrease.

The concept of pseudodiffusion-controlled reactions stimulates new approaches to a sustituent and solvent effect on reaction rate. In certain cases an increase of a susbtituent volume or an adhering of a solvent molecule to a reagent molecule may result only in a more severe steric constraint to a reaction controlled by diffusion. Concrete examples of such a behaviour have been found /3/.

Many pseudodiffusion-controlled reactions have been discovered recently. They are certain electron and proton transfer reactions, enzyme reactions, energy transfer, DNA recognition and binding, fluorescence quenching /2,9/. It has been shown recently that chemical anisotropy strongly affects reactivity of photogenerated radical pairs /10/.

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POLAROGRAPHIC STUDIES ON THE COPPER-ADENINE SYSTEM

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SUMMARY

The polarographic behaviour of adenine and of the copper-adenine system was studied in a medium of sulphuric acid.

It was found that adenine is irreversibly reduced at dropping mercury electrode (DME) and that its differential pulse polarography (DPP) peaks are suitable for the analytical determination of adenine concentrations.

In the presence of adenine, copper(II) ions are reduced in two consecutive steps indicating that adenine may complex with copper(I) ions, forming a species sufficiently stable in solution.

The influence of pH and of the concentrations either of copper(II) ions or adenine on the electrochemical reduction of the system were also studied.

1 - Introduction

Adenine (6-aminopurine) is one of the three most important components of nucleic acids, and is composed of a pyrimidinic nucleus attached to an imidazole nucleus.