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Binding and reactivity under restricted geometry conditions: Applicability of the Pseudophase Model to thermal and photochemical processes

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ABSTRACT

Reactivity under restricted geometry conditions can be quantitatively rationalized by using the Pseudophase Model. This model considers two states in equilibrium, free and bound, which are not perturbed by the reaction. That is, the reaction in which the two states participate must be slow in comparison to the exchange process between the free and bound states. This condition is fulfilled in the case of chemical reactions, but it does not hold for fast photochemical reactions. In spite of this, the Pseudo-phase Model was found to be, at least apparently, applicable for excited state reactions. However, a thorough analysis of the kinetic data brings to light important differences between the two types of reactions, particularly in the meaning of the parameters present in the equations of the Pseudophase Model.

1. Introduction

There is a growing interest in the study of reactions under restricted geometry conditions (r.g.c.); that is, under conditions in which the chemical species of interest are forced to remain, at least partly, associated to some receptors such as micelles and polymers [1••]. The r.c.g. imply a reduction of dimensionality and the physical conditions are generally quite different from those in the bulk phase. The binding of the chemical species and the receptors produces variations in the properties of both, the receptors and the ligands, and these changes can affect spectroscopic properties [2•,3••], catalysis [4,5•], and chemical and photochemical reactions [6–8•,9–11]. Results in this field can find applications in the design of chemical and biochemical sensors [12–14••,15••], synthetic methods [16], enzymatic reactions [17•], drug nanocarriers [18,19•], etc.

This review deals with the effects of r.g.c. on chemical and photochemical reactivity and with the applicability of the Pseudophase Model to the quantification of the kinetic data. If a significant part of the reactant (R) is associated to the receptor (M) the process can occur through two different paths:

$$\text{Path 1} \quad R_{free} \rightarrow \text{Products} \quad k_{free} \tag{1}$$

$$\text{Path 2} \quad R_{bound}(R/M = R_{bound}) \rightarrow \text{Products} \quad k_{bound} \tag{2}$$

When the reaction is slow compared to the kinetics of distribution of the reactant(s) between the free and bound states, this distribution can be considered at equilibrium. That is:

$$R_{free} + M \overset{K}{\rightleftharpoons} R_{bound}(R/M) \tag{3}$$

The reactant(s) free and bound states react at different rates because of variations in the free energies of the reactants, R, (and transition states) when they are bound to the receptor, M. As a consequence, catalytic effects are observed. For instance, in the case of bimolecular reactions, if the two reactants associate to the receptor, an increase in the local concentrations is caused and an increase in the reaction rate will follow [20••,21,22•,23]. Nonetheless, this effect cannot explain the differences in reactivity of the free and bound states in unimolecular reactions. In this case the differences must be related to the properties of the local reaction medium of the associated species, which is quite different from that surrounding the free reactant; that is, for instance, changes in the electric fields through solvent saturation effects, variations in the dielectric constant and dynamics of the solvent, etc. [24]. The effects of r.g.c. are not only limited to variations in the reaction rate, but changes in the products of the reaction can also be observed.

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This is the basis of their application in synthetic methods, as was mentioned above [16].

Elucidation of the r.g.c. effects in each particular case is a challenge, which makes this study relevant from a fundamental point of view. R.g.c. can be carried out under average conditions, not requiring usually complicated manipulation systems and many experimental techniques can provide information about the state of the free and bound species. It is a versatile method to catalyzed processes since external stimulus such as pH, ionic strength, light, magnetic fields, etc. can change drastically the structure of the receptors [25,26]. In the following sections a common formulation, based on the Pseudophase Model (or Two-State Model), for the r.g.c. effects on chemical and photochemical processes will be considered. Particular attention to the actual meaning of the parameters appearing in the kinetic equations will be paid. The final section presents the conclusions and perspectives.

2. A common formulation for chemical and photochemical reactions

The variations in the reaction rate observed under r.g.c. can be explained by the Pseudophase Model, and by other models such as the Olson-Simonson model [27], among others [28]. As was commented above, the reactants are supposed to be present in two states, free and bound, which are at equilibrium even if they participate in a reaction. This assumes that equilibrium 3 is much more rapid than the processes involving the free and bound states of R. Under these circumstances, R_{free} and R_{bound} can be expressed as:

$$[R_{free}] = \frac{1}{1 + K[M]}\,[R] \tag{4}$$

$$[R_{bound}] = \frac{K[M]}{1 + K[M]}\,[R] \tag{5}$$

The accumulation of different species at the surface or inside receptors is the consequence of a favorable binding Gibbs energy between the reactants (ligands) and the receptors. The change in the chemical potential of both, the ligand and the receptor, is shown through variations in their activity coefficients. The variation in the Gibbs energy of the reagent as a result of its union to the receptor is expressed as [29]:

$$\Delta G = RTln\gamma_R \tag{6}$$

where

$$\gamma_R = \frac{1}{1 + K[M]} \tag{7}$$

when the species and the receptor are present in the solution. In Eq. (7) K is the equilibrium constant corresponding to the process shown in Eq. (3). If free and bound states react at different rates, the observed rate constant can be written as:

$$k_{obs} = \frac{k_{free} + k_{bound}K[M]}{1 + K[M]} \tag{8}$$

which is the well-known equation of the Pseudophase Model.

The application of the above eqs. assumes that the association of the reactant to the receptor (Eq. (3)) must be at equilibrium. This requirement is usually fulfilled by thermal (ground-state) processes. However, as was mentioned above, in the case of photochemical reactions (excited states), this hypothesis does not always hold due to the lifetime of the excite state or to the rates of the forward and reverse processes in Eq. (3). For this reason, thermal and photochemical processes will be considered in different sections.

3. Reactivity under r.c.g. conditions with the participation of ground states reactants

3.1. Micellar solutions

The study of reactivity in direct and inverse micelles has been the goal of many researchers because they provide the possibility of the reactants to be localized in a variety of microenvironments, which permit to control the reaction rate of several processes such as oxidations, ligand substitution reactions, etc. [30,31]. Most of the reactions occurring in micellar solutions happen, at least partially, at the interfaces. However, an important feature of these interfaces is that they are highly anisotropic and, as a consequence, the observed variations in reactivity depend on the localization and orientation of the reactants at the interfacial regions. For instance, the dielectric constant of micellar interfaces are frequently estimated utilizing different probes [32••] and the results are used for explaining the observed changes in reactivity. However, this is only correct if the location at the interface of the probe and of the reactants is the same.

For a true unimolecular reaction the application of the Pseudophase Model renders Eq. (8). In the case of bimolecular reactions Eq. (8) is also valid if one of the reactants preferentially remains in the aqueous phase and one can write:

$$k_{obs} = \frac{k_{free} + k'_{bound}K[M]}{1 + K[M]} \tag{9}$$

The meaning of k_{free} is the same as in Eq. (8). If reactant A is the one associated to the micelles, k'_{bound} is related to the true second order rate constant, k^{bound}, as:

$$k'_{bound} = k^{bound}\kappa_A \tag{10}$$

where

$$\kappa_A = \frac{[A]_{bound}}{[A]} \tag{11}$$

Here [A] is the A concentration referred to the total solution volume and $[A]_{bound}$ is the A concentration in the interface, referred to the volume of this phase.

In the case that both reagents, A and B, are associated to the receptor, M, the following eq. should be considered in order to quantify the r.c.g. effects:

$$k_{obs} = \frac{k_{free} + k''_{bound}K_AK_B[M]}{(1 + K_A[M])(1 + K_B[M])} \tag{12}$$

where K_A and K_B are the equilibrium constants corresponding to the binding shown in Eq. (3) that involves the reactants A and B, respectively. k_{free} and k''_{bound} refer to the reaction taking place in the aqueous phase and in the micellar phase, the latter related to the true second order rate constant, k_{bound}, similarly as in Eq. (9). Eq. (12) shows that for low receptor concentrations a linear dependence of k_{obs} is usually observed, whereas for high receptor concentrations a quadratic dependence is found.

Eqs. (3), (8) and (12) have been used for several authors in the quantitative rationalization of kinetic data in micellar solutions. Some examples are the oxidation of paracetamol by water-soluble colloidal MnO_2 in the presence of anionic surfactants [33], the micellar effects on the reaction between an arenediazonium salt and 6-O-octanolyl-L-ascorbic acid [34], and the process between methyl 4-nitrobenzenesulfonate and bromide ions in cationic micellar solutions in water-organic solvent mixtures [35]. In some cases deviations from the behavior predicted by these eqs. were observed. For instance, in the case of charged reactants and ionic micelles, an increase in the