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Geometric Effects of Reduction of Dimensionality in Interfacial Reactions[1]

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Abstract: The specific rate of a chemical reaction taking place at an interface may be different from that of the analogous reaction in a homogeneous phase, because of geometric and energetic reasons. The geometric effects of the localization (on the surface of large particles) of one of the reactants in a bimolecular elementary reaction are analyzed by using collision, transition-state, and diffusion-control theories. The geometric effects of the reduction of dimensionality are shown to be a significant decrease of the specific rates. Explicit expressions for the rate reduction and the interfacial rate constants are presented.

The rate of many chemical reactions is different when the reactions take place at an interface as compared to that of the analogous reactions in a homogeneous phase, at the same temperature. If the rate increases, the acceleration of a desired reaction is exploited in a variety of heterogeneous catalytic processes, many enzymatic reactions, micellar catalysis,[2] membrane mimetic systems,[3] etc. Naturally, the primary diagnosis for catalysis is provided by the comparison of the specific rates k^* and k, observed in the heterogeneous and homogeneous systems, under similar conditions, respectively. There can be several reasons for the change of the rate constant at an interface, which may broadly be classified as energetic, and "other" reasons. The first group involves the change of the potential energy surface of the reaction, which may also result in a reduction of the activation energy E_a. The other group encompasses changes in situations that are essentially geometric in nature: the relative arrangement, accessibility, and orientation of reactants and the dimensionality of space of their motion.

The theoretical calculation of the activation energy is possible only for a few of the simplest, homogeneous, gas-phase reactions. Nevertheless, the geometric effects at interfaces can be analyzed on simple model systems, using basic theories. The reduction of dimensionality of diffusion at interfaces, for example, has been shown by Adam and Delbrück to significantly contribute to rate enhancement, under favorable circumstances.[4] In fact, reduction of dimensionality seems to be nature's trick to overcome the barrier of diffusion control and make certain biochemical processes at low concentrations more efficient. In another study, Richter and Eigen investigated diffusion control for nonspherical geometry.[5,6] They analyzed the factors that influence the rate of reaction between a reactant and a specific site on the surface of a macromolecule. They found that if surface diffusion on the surface of the macromolecule is sufficiently fast, the largest linear dimension of the macromolecule carrying the target site can become decisive for the overall diffusion-controlled rate constant.[5,6]

In the present paper we shall investigate another geometric effect which is caused by the localization of one of the reactants of a bimolecular elementary reaction on a neutral surface with various geometries. The localization can be achieved by adsorption or chemical binding onto the surface of suspended particles. The analysis will be based on the collision, transition-state, and diffusion-control theories of reaction rates. Explicit expressions will be presented for the relative values of the rate constants on the surface and in homogeneous solution k^*_f/k_f. If the activation energies in the heterogeneous and homogeneous cases are the same, and if the possibility of surface diffusion is excluded, the reaction at the interface will be shown to be always slower than the analogous homogeneous reaction. Thus, the primary geometric effect of the reduction of dimensionality is a *decrease* of the specific rate.

The motivation for the study was provided by the apparent discrepancies found between the observed and expected diffusion-controlled rate constants of reactions such as proton transfer and ion-pair formation occurring at the surface of colloidally dispersed spherical metal oxide particles.[7-11] The analysis of the experimental findings in view of the theories developed in the present article will be presented in a forthcoming paper.[12] The conclusions reached in this paper are helpful not only for the correct classification of diffusion-controlled interfacial rates but also for the understanding of the functioning of immobilized enzyme,[13] chromatographic, ion-exchange, and solar energy conversion[14] processes.

Discussion

Let us consider the elementary reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_f} \mathrm{C} \tag{1}$$

taking place in a homogeneous liquid or gas phase. If B is localized (e.g., by adsorption at a solid-liquid or solid-gas interface), the corresponding heterogeneous reaction can be written as

$$\mathrm{A} + \mathrm{B_s} \xrightarrow{k^*_f} \mathrm{C_s} \tag{2}$$

where B_s represents the reactive surface site and C_s the reacted surface moiety, i.e., the surface-bound product. We wish to compare the forward rate constants k_f and k^*_f of the homogeneous and the heterogeneous reactions, respectively, focusing our attention solely on the effect of localization of B at the interface. Although most of the general ideas that will be used are also valid

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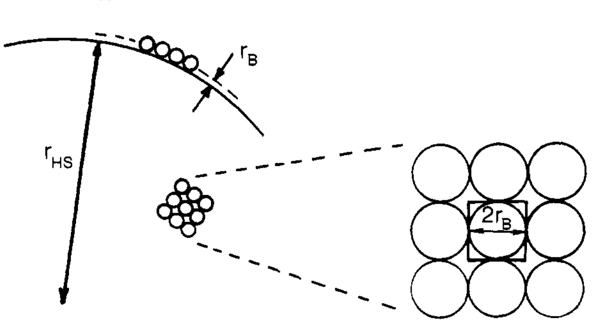

Figure 1. Schematic representation of the localization of B's on the surface of large hard spheres.

for solid–gas, gas–liquid (aerosols and bubbles), liquid–liquid (as in micellar systems), and solid–liquid interfaces, for simplicity, we shall focus our attention on the last. For the solvent we shall assume it to be an isotropic continuum.

The rate of homogeneous reaction 1 is typically given in the form

$$-\mathrm{d}c_A/\mathrm{d}t = k_f c_A c_B \quad (3)$$

and the rate constants by the Arrhenius equation

$$k = \chi \exp(-E_a/RT) \quad (4)$$

where χ is the preexponential factor into which frequency and steric factors are incorporated.[15] The other symbols have their customary meanings. Implicit in the formulation of (3) is the assumption that the concentrations c_i are uniform throughout the system at all times during the reaction. This assumption is quite valid so long as the activation energy E_a is appreciable, causing the reaction to be sufficiently slower than diffusion. If this is the case, collision and transition-state theories can be used for the comparison of k_f and k^*_f. If, on the other hand, E_a is very small, A will be consumed by B (and vice versa) faster than it can be replenished by diffusion, resulting in an average concentration gradient of the reactants around each other. In this case diffusional transport becomes rate limiting, and thus diffusion-control theories will be used for the analysis.

Physical Model. For the comparison of the forward specific rates of reactions 1 and 2, we shall first specify the homogeneous system. Then we shall alter the system in such a way that it corresponds to eq 2 and derive the theoretical expressions for the rate constant k^*_f.

The homogeneous system of volume V (cm^3) consists of molecularly dispersed N_A A's and N_B B's, hence the concentrations are $c_i = N_i/V$ (molecules/cm^3). The solution is sufficiently dilute that it can be considered ideal.

The heterogeneous system is identical with the homogeneous one, except now all N_B B molecules are packed as a continuous monolayer on the surface of neutral hard spheres (HS) of radius r_{HS}. The transition from the homogeneous to the heterogeneous case emulates the adsorption (or binding) of B on the surface of monodispersed colloidal particles or (with a minor modification of the theoretical conclusions) the sudden aggregation of B to monodispersed colloidal particles, prior to reaction. As to the way of packing B on the surface of the hard spheres, instead of considering possible unique arrangements we only insist that the hard spheres be much larger than B or A, i.e., $r_{HS} \gg r_B$ and $r_{HS} \gg r_A$, and that A be larger than any gap between the B's. The last requirement assures that any collision between A and the large particle represents a contact only between A and B. An easily tractable arrangement, for which the calculations will be presented, is shown in Figure 1. In this arrangement, the total area of the hard spheres equals the total target area presented by the B's for A

$$4\pi r_{HS}^2 N_{HS} = (2r_B)^2 N_B \quad (5)$$

as the radius of the hard sphere is not increased significantly by the presence of B's on the surface. With relationship 5 in mind, one of our primary objectives is to examine the dependence of k^*_f on the choice of r_{HS} (and N_{HS}).

Rate of Reaction according to Collision Theory. For homogeneous reaction 1, simple collision theory provides the rate to be[16]

$$-(\mathrm{d}N_A/\mathrm{d}t) = N_A N_B V^{-1}[(8\pi kT/\mu_{AB})^{1/2}\sigma_{AB}^2 \exp(-E_a/kT)] \quad (6)$$

where σ_{AB}^2 is the "effective" collision cross section, and $\mu_{AB} = m_A m_B/(m_A + m_B)$ is the reduced mass of A and B. This theory assumes that the reactant molecules are distributed uniformly throughout the available volume at all times. If we assume that only very short range interaction exists between A and B (a minimum requirement for reaction), but otherwise they follow hard-sphere dynamics, then the

$$\sigma_{AB}^2 \approx (r_A + r_B)^2 \quad (7)$$

substitution can be made in (6). The quantity in brackets in (6) is of course the rate constant k_f of reaction 1 in units of cm^3 molecule^{-1} s^{-1}. The quantity $k_f/[\exp(-E_a/kT)]$ is the collision constant that represents the limiting value of k_f in either case where $E_a \rightarrow 0$ or/and $T \rightarrow \infty$.

Now, for the heterogeneous system 2, as specified in the previous section including eq 5, the number of collisions between A and the hard spheres (covered with B's) is given by

$$Z_{A\text{-}HS} = N_A N_{HS} V^{-2}(8\pi kT/\mu_{A\text{-}HS})^{1/2}(r_A + r_{HS})^2 \quad (8)$$

where the reduced mass $\mu_{A\text{-}HS}$ of A and HS is $\mu_{A\text{-}HS} \approx m_A$ since $m_{HS} \gg m_A$, and $(r_A + r_{HS})^2 \approx r_{HS}^2$. With the use of eq 5 and 8, for the rate of reaction 2 we find

$$-\mathrm{d}N_A/\mathrm{d}t = N_A N_B V^{-1}[(8kT/\pi m_A)^{1/2} r_B^2 \exp(-E^*_a/kT)] \quad (9)$$

where E^*_a is the activation energy of heterogeneous reaction 2, and the expression in brackets is k^*_f. Hence, from (6), (7), and (9), the ratio of the rates is found to be

$$k^*_f/k_f = \pi^{-1}[m_B/(m_A + m_B)]^{1/2}[r_B/(r_A + r_B)]^2 \exp(-\Delta E_a/kT) \quad (10)$$

where $\Delta E_a = E^*_a - E_a$ is the difference between the activation energies in the heterogeneous and homogeneous cases, respectively, which of course is usually not zero. The exponential term represents the energetic reason for the change of the specific rate upon reduction of dimensionality. The factors π^{-1} and $[r_B/(r_A + r_B)]^2$ are expressions of the relative geometrical constraints on the heterogeneous system, i.e., that with respect to a single B on the surface, the A–B collisions are restricted from virtually all other than frontal direction. Although the radius of A is quite irrelevant for the heterogeneous rate from eq 9, the ratio k^*_f/k_f in (10) is clearly a function of the relative values of r_A and r_B. The factor $[m_B/(m_A + m_B)]^{1/2}$ arises from the localization of B on the hard sphere whose average speed is much smaller than that of B in the homogeneous case. Clearly, all but the exponential factor are smaller than unity, indicating that the geometrical contributions to the specific rate upon reduction of dimensionality are negative. In fact, for reasonable molecular parameters (where the sizes and masses of A and B are similar), the activation energy of the surface reaction needs to be lower than that of the corresponding homogeneous reaction by 2.5 to 7.5 kJ/mol, just to compensate for the rate reduction cuased by steric and mobility factors. Disregarding the activation energy term, simple considerations result in a maximum 50-fold estimated decrease of rate by the geometric factors upon reduction of dimensionality. Interestingly, collision theory predicts no explicit rate dependence on the radius of the hard spheres on which B's are localized (see eq 9 and 10).

If the closest hexagonal packing is used, more B can be loaded on the surface of the hard spheres than in the arrangement of

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Figure 1. In this case either less hard spheres of the original size or the original number with smaller r_{HS} are needed to accommodate all the B's. In any event, the collision number Z_{A-HS} in (8) becomes smaller, increasing the geometric rate reduction effect of the localization of B's.

If incomplete coverage of the hard spheres is permitted (where only a fraction $\alpha < 1$ of their surface is randomly occupied by B's) by increasing r_{HS} at fixed N_{HS}, the relative rate will be unchanged and given by eq 10.

Rate of Reaction according to Transition-State Theory. Transition-state theory[17] assumes the formation of an activated complex $X_{\ddagger}$ during the course of the reaction along the reaction coordinate, and thus the forward reactions in homogeneous reaction 1 and heterogeneous reaction 2, close to equilibrium, can be written as

$$A + B \rightleftharpoons X^{\ddagger} \xrightarrow{k_f} C \tag{11}$$

and

$$A + B_s \rightleftharpoons X_s^{\ddagger} \xrightarrow{k^*_f} C_s \tag{12}$$

respectively. $X_s^{\ddagger}$ represents the activated complex in the surface reaction.

In the homogeneous case, Eyring provides the expression for the rate constant as

$$k_f = \kappa \frac{kT}{h} \frac{F_{\ddagger}}{F_A F_B} \exp(-E_0/kT) \tag{13}$$

where κ is the transmission coefficient (usually $\kappa \approx 1$), the F's are the molecular partition functions of the various species, and the other symbols have their usual meanings. E_0 is the difference between the zero-point energy of the activated complex and that of the reactants, i.e., the hypothetical energy of activation at 0 K. The partition functions F can be factorized into contributions corresponding to translational, rotational, vibrational, and electronic energy:

$$F = f_{tr} f_{rot} (\prod_j f_{vib,j}) f_{el} \tag{14}$$

where the vibrational partition function $f_{vib,j}$ for each normal mode j of vibration of a species is included. For moderate conditions, $f_{el} \approx 1$. If B is immobilized on the surface of hard spheres, the values of the partition functions f of B and $X^{\ddagger}$ change, lowering the rate constant of reaction 12 as compared to that of reaction 11. Several authors have previously derived rate equations for bimolecular reactions occurring at surfaces using transition-state theory.[17-19] All of these treatments, however, were dealing with mechanisms of the Langmuir–Hinshelwood type, which involves the adsorption of *both* reactants onto the surface at adjacent sites followed by subsequent reaction:

$$A_s + B_s \rightarrow C_s \tag{15}$$

The mechanism of our interest (eq 2 and 12) is referred to as the Langmuir–Rideal mechanism[18] that seems to be less common than the Langmuir–Hinshelwood type in heterogeneous catalytic processes.

Our reaction in (2) and (12) is formally identical with adsorption of A to discrete surface sites, the rate of which has been treated previously.[20] We shall augment the arguments used and recast the result in a form amenable to facile comparison with expression 13 for the analogous homogeneous reaction in (1) and (11).

Clearly, the actual expression for the rate constant k_f in (13) depends on the chemical structure of the reactants. We shall look at the simplest case only, where both A and B are atoms but where the geometric effect of the reduction of dimensionality already becomes apparent. In this case, A and B have only a translational degree of freedom and the diatomic activated complex has both translational and rotational degrees of freedom (the decomposition vibration is factored out). If we approximate the A–B bond length in $X_{\ddagger}$ by $(r_A + r_B)$, the moment of inertia in the expression for $f_{rot,\ddagger}$ becomes

$$I_{\ddagger} = (r_A + r_B)^2 m_A m_B/(m_A + m_B) \tag{16}$$

and we find

$$k_f = \kappa[8\pi kT(m_A + m_B)/m_A m_B]^{1/2}(r_A + r_B)^2 \exp(-E_0/kT) \tag{17}$$

Except for κ, the result is identical with that obtained by using the collision theory (cf. eq 6 and 7). Equation 17 can also be written as

$$k_f = \kappa \frac{kT}{h} \frac{f_{tr,\ddagger} f_{rot,\ddagger}}{f_{tr,A} f_{tr,B}} \exp(-E_0/kT) \tag{18}$$

The rate constant for the surface reaction can easily be obtained from (18) by accounting for the changes in the partition functions caused by the localization of B on the hard sphere, which leads to the following substitution:

$$f_{tr,\ddagger} \approx f_{tr,HS} \qquad f_{rot,\ddagger} \approx f_{rot,HS} \qquad f_{tr,B_s} \approx f_{tr,HS} \tag{19}$$

since the presence of B's and $X^{\ddagger}$'s on the hard sphere represents a negligible perturbation on its mass and size. Although B_s and $X_s^{\ddagger}$ each have an additional vibrational degree of freedom, the corresponding partition functions f_{vib,B_s} and $f_{vib,\ddagger}$ are unity at moderate temperatures. Hence, with the substitutions in (19), the heterogeneous rate constant becomes

$$k^*_f = \kappa^* \frac{kT}{h} \frac{f_{tr,HS} f_{rot,HS}}{f_{tr,A} f_{tr,HS} f_{rot,Hs}} \exp(-E^*_0/kT) \tag{20}$$

$$= \kappa^* \frac{kT}{h} f_{tr,A}{}^{-1} \exp(-E^*_0/kT) \tag{21}$$

The rotational partition function of B_s

$$f_{rot,B_s} \approx f_{rot,HS} \tag{22}$$

in the denominator in eq 20 must be included, because B attached to the surface also has a rotational degree of freedom in contrast to the homogeneous case. However, due to the large size and mass of the hard sphere to which they are attached, B_s and $X^{\ddagger}{}_s$ became very similar in their mobilities. This leads to the approximations in eq 19 and 22 and the cancellations in eq 20.

The ratio k^*_f/k_f is obtained from (18) and (21) as

$$k^*_f/k_f = (\kappa^*/\kappa)(f_{tr,B}/f_{tr,\ddagger} f_{rot,\ddagger}) \exp(-\Delta E_0/kT) \tag{23}$$

where $\Delta E_0 = E_0 - E^*_0$ is the difference of the activation energies in the homogeneous and heterogeneous cases. The exponential factor together with the ratio of the transmission coefficients (κ^*/κ) represent the energetic effects, and the factor involving the partition functions the geometric effect of the reduction of dimensionality. The major effect of the localization of B is that both B and $X^{\ddagger}$ assume the mobility of the bulky hard sphere, which makes them and their translational and rotational partition functions very similar. These lead, in the framework of transition-state theory, to a significant lowering of the rate. With use of typical numerical values for the partition functins in (23), the geometric effect represents an estimated 10- to 100-fold decrease of the specific rate. Just to make up for this rate loss, the activation energy of the heterogeneous reaction needs to be about 10 kJ/mol lower than that of the analogous homogeneous reaction.

For more complicated reactions, e.g., where A is a diatomic molecule and $X_{\ddagger}$ is a nonlinear triatomic species, the geometric rate reduction can be as large as 10^3-fold.

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The Rate of Reaction according to Diffusion-Control Theory. In many fast reactions in solution, where the intrinsic rate of reaction is higher than that of diffusive transport, the random spatial distribution of A and B is not maintained during reaction and an average concentration gradient of the reaction partner arises around each molecule. A rigorous probabilistic treatment for the emergence of the gradient was given by Collins and Kimball.[21] In such a case of course the diffusion of A toward B (assumed to be fixed in space, at this point) becomes rate limiting, and in the absence of long-range interaction between the reactants Fick's first

$$\Phi = -\mathcal{A}D_A\,\partial c_A/\partial r \tag{24}$$

and second laws

$$\partial c_A/\partial t = D_A(\partial^2 c_A/\partial r^2 + 2\partial c_A/r\partial r) \tag{25}$$

written for spherical symmetry around the center of B can be used as the basis for the derivation of expressions for diffusion-limited rates. Many authors[22-26] have done so, using a number of different boundary and initial conditions.

With use of the steady-state approximation $\partial c_A/\partial t = 0$ and realizing that then the average net flow Φ of A entering perpendicularly through any spherical surface (of area $\mathcal{A}$) concentric with B is constant (the exact boundary condition corresponding to this is the so-called radiation-boundary condition),[21] $c_{A,R}$ can be calculated from (24) and (25) as

$$c_{A,R} = c_{A,\infty} - \Phi/4\pi DR \tag{26}$$

where the simultaneous diffusion of *both* reactants is taken care of by introducing their relative diffusion coefficient $D = D_A + D_B$. R in (26) is the "reaction radius" = $r_A + r_B$, and $c_{A,\infty} = \lim_{r\to\infty} c_{A,r}$ represents the analytical bulk concentration of A. Since the rate of reaction between A and B is

$$\text{rate} = k_f c_{A,R} c_{B,\infty} \tag{27}$$

Noyes[23] obtained the expression for the effective rate constants $k_{f,eff}$ in the steady state as

$$k_{f,eff} = \frac{k_f}{1 + \dfrac{k_f}{4\pi RD}} = \frac{4\pi RD}{1 + \dfrac{4\pi RD}{k_f}} \tag{28}$$

This is essentially the Smoluchowski equation[22] without the time-dependent term, which is negligible after about 10^{-7} s. Later, Debye[27] included the effect of electrostatic potential acting between the reactants, and Eigen[28] also derived an equation for diffusion-controlled dissociation-rate constants.

For our present analysis, we shall concentrate on the simple case when $k_f \gg 4\pi RD$ in (28), then the diffusion-controlled specific rate simplifies to

$$k_{f,eff} \approx 4\pi RD \tag{29}$$

This corresponds to B essentially being a sink for A, i.e., $c_{A,R} = 0$. With the use of the Stokes–Einstein relation for the diffusion coefficient

$$D_i = kT/6\pi r_i \eta \tag{30}$$

(where η is the viscosity of the medium) and substituting the difinitions of R and D into (29), we obtain for the diffusion-controlled rate constant in homogeneous solution

$$k_{f,eff} = 4\pi(r_A + r_B)\frac{kT}{6\pi\eta}(r_A^{-1} + r_B^{-1}) = \frac{2}{3}\frac{kT}{\eta}\frac{(r_A + r_B)^2}{r_A r_B} \tag{31}$$

In the heterogeneous case, where B's are localized on hard spheres, the "sink property" of B is transferred to the large particles and $k^*_{f,eff}$ can immediately be obtained from (31)

$$k^*_{f,eff} = \frac{2}{3}\frac{kT}{\eta}\frac{(r_A + r_{HS})^2}{r_A r_{HS}} \tag{32}$$

To elucidate the geometric effect of reduction of dimensionality, however, now we have to enforce the conditions specified for the physical model. With eq 31 and 32 the forward rates of reactions 1 and 2 are

$$-\mathrm{d}c_A/\mathrm{d}t = \left[\frac{2kT(r_A + r_B)^2}{3\eta r_A r_B}\right]c_{A,\infty}N_B/V \tag{33}$$

and

$$-\mathrm{d}c_A/\mathrm{d}t = \left[\frac{2kT(r_A + r_{HS})^2}{3\eta r_A r_{HS}}\right]c_{A,\infty}N_{HS}/V \tag{34}$$

respectively. By invoking condition 5 and if, as previously, $r_{HS} \gg r_A$, the heterogeneous rate in (34) becomes

$$-\mathrm{d}c_A/\mathrm{d}t = \left[\frac{2kT}{3\pi\eta}\frac{r_B^2}{r_A r_{HS}}\right]c_{A,\infty}N_B/V \tag{35}$$

Notice that the inverse relationship between r_{HS} and the rate in (35) is not simply an expression of obtaining larger surface area by using smaller hard spheres, since the total surface area is fixed by r_B and N_B according to condition 5. The result rather is due to the lowering of the number and thus the concentration of the hard sphere sinks with increasing r_{HS}.

The factors in brackets on the right side of eq 35 and 33 represent the actual diffusion-controlled heterogeneous k'^*_f and homogeneous k'_f specific rates, respectively, which are to be compared. The ratio of the rates

$$k'^*_f/k'_f = r_B^3/\pi r_{HS}(r_A + r_B)^2 \tag{36}$$

is clearly much smaller than one. With use of typical atomic radii for r_A and r_B and colloidal size ($r_{HS} = 1$ μm) for the large particle, the ratio is about 10^{-5}. Obviously, the decrease of rate caused by the geometric effects of reduction of dimensionality is more pronounced for diffusion-controlled than for slow reactions. Of course, the effect is strongly dependent on r_{HS}. In fact, in the limiting case when all B's are packed on a single large hard sphere, its radius according to eq 5 must be

$$r_{HS} = r_B(N_B/\pi)^{1/2} \tag{37}$$

and the heterogeneous rate in (34) becomes

$$-\mathrm{d}c_A/\mathrm{d}t \approx \frac{2kT}{3\eta\pi^{1/2}}\frac{r_B}{r_A}c_{A,\infty}N_B^{1/2}/V \tag{38}$$

by realizing that $r_A \ll N_B^{1/2}$ during the derivation. Interestingly, the low-end limiting heterogeneous rate is proportional to the square root of N_B. The ratio of the heterogeneous and homogeneous rates in this case,

$$\frac{r_B^2}{\pi^{1/2}(r_A + r_B)^2 N_B^{1/2}} \tag{39}$$

is obviously a very small number.

It is also illustrative to investigate the relative "sink strength" of a hard sphere covered with B and that of a B in the homogeneous solution, in terms of the corresponding net flow of A. Using eq 26, and by enforcing the same boundary conditions in

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the homogeneous and heterogeneous cases, we find

$$\frac{\Phi^*}{\Phi} = \frac{4\pi D^* R^*(c_{A,\infty} - c_{A,R^*})}{4\pi DR(c_{A,\infty} - c_{A,R})} \approx \frac{r_{HS} r_B}{(r_A + r_B)^2} \qquad (40)$$

since $c_{A,R} = c_{A,R^*} = 0$ and $r_{HS} \gg r_A, r_B$. Clearly, a hard sphere covered with B represents a more effective sink that an individual B, in spite of the much smaller diffusion coefficient of the large particle. Nevertheless, as r_{HS} is increased, the hard-sphere concentration decreases faster (by $1/r_{HS}^2$, from eq 5) than the sink strength increases, leading to the net rate reduction given in (36).

A straightforward extension of the ideas pursued would be to investigate the effect of $r_{HS} \rightarrow \infty$, i.e., the localization of B's on a flat surface. In this case, however, one deals with the problem of one-dimensional diffusion described by Fick's laws in Cartesian coordinates, where no steady state is possible for finite bulk concentration $c_{a,\infty}$ and time. This is of course expected, since setting $\partial c_A/\partial t = 0$ implies $\partial c_A/\partial x =$ constant, which is possible only for $c_{a,\infty} \rightarrow \infty$ or $\partial c_A/\partial x = 0$. The first case is physically not feasible, and the latter one applies only for slow reactions. Thus no direct comparison can be made.

Summary

The primary, geometric effect of localizing one of the reactants on the surface of large particles (hard spheres) in a bimolecular elementary reaction is the decrease of the rate. We normalized the conditions such that the homogeneous and the interfacial rates could directly be compared by using collision and transition-state theories for the slow and diffusion-control theory for the fast reactions. The essence of the normalization is that the bulk concentration of the reactants is kept constant in the transition from the homogeneous to the heterogeneous case, and the concentrations of the interfacial species are described in the normal bulk number-density units, since the hard spheres are randomly distributed over the space available. In the heterogeneous case, the B molecules and the activated complex $X^‡$ bound to the surface lose a major fraction of their degrees of freedom and assume the mobilities of the bulky hard sphere. If the hard spheres were randomly distributed but fixed in space (as in a chromatography or ion-exchange packing), the decrease of the specific rate would be even greater than found in our treatment. In spite of the high local concentrations caused by the clustering of B on the hard spheres, the associated negative geometric effects of the reduction of dimensionality are dominant, leading to a significant rate reduction, especially for diffusion-controlled reactions. Consequently, reactions taking place on the surface of colloidal particles and having a Langmuir–Rideal type mechanism with a rate constant of as small as 10^5–10^4 M^{-1} s may be classified as diffusion controlled. For such a system, the upper limit of the diffusion-controlled rate constant in the usual units can be estimated from

$$k = \frac{2kTL}{3\pi\eta 1000}\frac{r_B^2}{r_A r_{HS}} \ (M^{-1}\ s) \qquad (41)$$

which follows from eq 35, and where L is Avogadro's number.

For "reaction-controlled" rates, the geometric rate reduction is independent of the size of the hard spheres, according to the collision (eq 10) and the transition-state (eq 23) theories. For diffusion-controlled reactions, however, the size of the rate reduction increases with r_{HS} (eq 36).

For slow reactions, it is important to realize that for successful Langmuir–Rideal-type heterogeneous catalitic acceleration, the interfacial reaction needs to have an activation energy at least 10 kJ/mol lower than that of the homogeneous reaction just in order to compensate for the geometric rate reduction, in the absence of surface diffusion.

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$2_s + 2_s$ Reactions at Transition Metals. 1. The Reactions of D_2 with Cl_2TiH^+, Cl_2TiH, and Cl_2ScH

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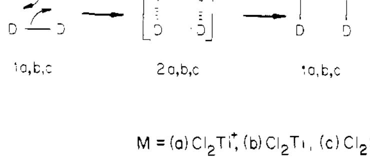
Abstract: With use of ab initio electronic structure theory, activation energies and transition-state geometries have been found for the exchange of the title transition-metal hydrides with D_2. These calculations indicate that such concerted, suprafacial [2 + 2] reactions proceed at low energy if the M–H bond is nonpolar and covalent, and if this bond uses mostly valence d-orbital character on the metal.

The Woodward–Hoffmann orbital symmetry rules have had a profound effect on the understanding of organic reactions,[1] but attemps to generalize these rules to organic reactions mediated by transition metals have not led to specific results of comparable utility.[2] It is generally assumed that there are no particular reactions that are symmetry forbidden for transition-metal systems. For example, $[2_s + 2_s]$ reactions such as migratory insertion pervade organometallic chemistry,[3] whereas analogous reactions are known to be forbidden in strictly organic systems. Our belief (vide infra) is that the detailed nature of the metal–hydrogen and metal–carbon *covalent* bond is critical to the process of these now allowed reactions. An appreciation of the transition-metal–ligand covalent bond is now emerging[4] that allows us to go beyond the simple standards of allowed and forbidden and to begin predicting

Scheme I



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