

## General Phenomenological Analysis of Activation, Diffusion, and Pseudodiffusion Control

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A phenomenological kinetic analysis of a general bimolecular association  $A + B = C$  in solution shows that the criteria for activation and diffusion control are different and provides a basis for a generalized concept of pseudodiffusion control.

For a bimolecular reaction in solution, rate constants  $k$ ,  $k_D$ , and  $k_A$  describe the actual rate and those which would be realized under diffusion and activation control. A reaction can be 'pseudodiffusion controlled,'  $k = k_{\psi D}$ , where  $k_{\psi D}$  is less than  $k_D$  but may parallel it in responses to variations in viscosity and temperature. Examples of pseudodiffusion controlled radical-radical reactions have been provided and discussed recently by Burshtein *et al.*<sup>1</sup> If equation (1) [instead of equation (2), which is often presented]<sup>2</sup> is correct for the general case (that is, for any molecular shapes, spins, conformations, *etc.*), then pseudodiffusion control results when  $bk_A \gg k_D$  and  $b > 1$ .

$$k = k_D k_A / (k_D + bk_A) \quad b \geq 1 \quad (1)$$

$$k = k_D k_A / (k_D + k_A) \quad (2)$$

$$k = k_{\psi D} = k_D/b \quad bk_A \gg k_D \quad b > 1 \quad (3)$$

While equations different from (2) have been derived for specific models,<sup>3</sup> no proof of equation (1) has been given for the general case. The following phenomenological kinetic analysis provides both a proof and a physical interpretation of the parameter  $b$ , thereby generalizing both the theoretical framework and the concept of pseudodiffusion control.

Consider a bimolecular association  $A + B = C$ . A first collision of a previously uncorrelated A and B gives an associated pair that may suffer many subsequent collisions before reacting or separating permanently. Define 'engagement' as the sequence of events beginning with the first collision and ending with reaction or permanent separation.<sup>4</sup> Let  $a$  be the probability that an engagement leads to reaction. Since the effective lifetimes of associated pairs are of the order of  $10^{-9}$  s,<sup>5</sup> they can be treated as steady-state intermediates and the forward rate,  $k[A][B]$ , can be expressed as the product of the engagement rate,  $k_D[A][B]$ , and the reaction probability  $a$  (equation 4). Similarly, the backward rate  $\bar{k}[C]$  is the product of the bond cleavage rate  $\bar{k}_A[C]$  and  $1 - \bar{a}$ , where  $\bar{a}$  is the probability of geminate recombination. Kinetic and thermodynamic considerations require equations (6), where  $K$  is the equilibrium constant. Equations (5) and (6) lead to equation (7). Let  $b$  be  $\bar{a}/a$ . Then equation (1) results by eliminating  $a$  and  $\bar{a}$  from equations (4) and (7).

A well-known example to the contrary shows that  $b = 1$  ( $a = \bar{a}$ ) is not true in general, so that equation (2) cannot be true in general. Electron spins of radicals can give contributions to  $a$  and  $\bar{a}$  of factors of 1/4 and 1 because engaged AB pairs have 25% initial singlet character while geminate pairs (from singlet C) are initially 100% singlet.<sup>1,6</sup>

$$k = ak_D \quad (4)$$

$$\bar{k} = (1 - \bar{a})\bar{k}_A \quad (5)$$

$$K = k/\bar{k} = k_A/\bar{k}_A \quad (6)$$

$$k = (1 - \bar{a})k_A \quad (7)$$

That  $b \geq 1$  follows from a general argument. The initial state of a geminate AB pair is optimal for combination. If some other state of AB were more reactive in combination, then there would exist at equilibrium a net cyclic reaction flow in which C dissociates to a less reactive AB pair, which then converts into a more reactive pair that recombines to C, violating the principle of detailed balance. Since engaged AB pairs are not necessarily equivalent to geminate pairs,  $a$  is not necessarily equal to  $\bar{a}$ , and if not, then  $a$  must be less than  $\bar{a}$ .

That the values of different parameters,  $a$  and  $\bar{a}$ , are criteria for diffusion (equation 4) and activation control (equation 7) is especially significant. An  $a$ -value near unity implies diffusion control, while an  $\bar{a}$ -value much less than unity implies activation control, but a small  $a$ -value does not imply activation control nor is diffusion control necessarily implied by a value of  $\bar{a}$  which is close to unity. Pure pseudodiffusion control occurs if, and only if,  $a$  is less than  $\bar{a}$  and  $\bar{a}$  tends to unity, as shown by equation (8), which follows from equation (4) and the definitions of  $b$  and  $k_{\psi D}$ . Near pseudodiffusion control occurs when  $k_D$  and  $bk_A$  are comparable ( $\bar{a}$  is less than but comparable to unity) and  $b > 1$ .

$$k = \bar{a}k_D/b = \bar{a}k_{\psi D} \quad b > 1 \quad (8)$$

The response of  $k_{\psi D}$  to viscosity change will parallel that of  $k_D$  only when  $b$  is viscosity independent. Both  $a$  and  $\bar{a}$  will, in general, be viscosity dependent, but often their dependencies may be parallel, so that  $b$  is viscosity independent or nearly so over some range.

The view of pseudodiffusion control given here is broader than that of Burshtein *et al.*, who concentrated on molecular rotational orientational effects and did not include spin effects in radical-radical reactions as possible contributors.<sup>1</sup> In the present analysis, spin, orientational, and other effects that can make  $\bar{a}$  greater than  $a$  are on the same footing.

Sufficiently rapid associated pair relaxation will make engaged and geminate pairs equivalent, effectively, so that  $a = \bar{a}$ ,  $b = 1$ , and there can be no pseudodiffusion control. For this case, not only must relaxation be complete within effective associated pair lifetimes, it must also be complete before significant collapse to C occurs. When A and B are extremely reactive, geminate pair relaxation would have to be very fast indeed, with relaxation times of the order of  $10^{-11}$  or  $10^{-12}$  s, or even less, in order to prevent pseudodiffusion control.

Of course, pseudodiffusion control may not occur because other factors make engaged and geminate pairs equivalent. For example, if A and B are spin-free spheres, so that there can be no spin, orientational, or conformational differences between engaged and geminate pairs, then  $b = 1$  and pseudodiffusion control is not possible.

Very large effects can, in principle, originate in conformational factors. Consider a case in which the residue of A and C is forced to adopt a conformation A' that is not preferred for free A. When C cleaves, a geminate pair A'B results, where A' has a high-energy conformation. If the conformational relaxation time of A is much longer than the effective lifetimes

(ca.  $10^{-9}$  s)<sup>5</sup> of associated pairs, but shorter than the mean lifetimes of free A molecules, then conformational equilibrium will be (nearly) established in the free A population. Under these conditions only collisions of A' with B can lead to C. If a fraction  $f$  of the free A population exists as A', then  $a$  (but not  $\bar{a}$ ) is reduced by a factor  $f$ , providing a contribution to  $b$  of  $1/f$ , which could be many orders of magnitude greater than unity.

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