Competitive effects on the rate of the diffusion-controlled reaction A+B→C*

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The effects of competition among the reactants in the diffusion-controlled bimolecular reaction A+B→B were recently examined in companion articles in this Journal.1,2 The treatment presented in these papers was based on an analogy taken from electrostatics, and resulted, after substantial analysis, in a description of the reaction kinetics which accounts for various correlations among the reactants. A primary conclusion of the first of these papers1 (herein referred to as FD) was that the effective rate coefficient for the reaction is enhanced over the value predicted by simpler models which ignore competitive effects. Furthermore, it was demonstrated in FD that the enhancement, to first order, varied explicitly as the square root of the B species (called "sink" in FD) concentration, a result which differed from the concentration dependence elicited elsewhere by other techniques3,4 (see Ref. 14 of FD). As was pointed out in FD (Refs. 4, 6, 7, and 8), others have attempted to include correlations in their discussions of diffusion-controlled reactions. With this in mind, the readers of FD may be interested to note that a treatment of the same problem in terms of a Waite-type formalism5 leads to the same square root dependence in this system can be accounted for through the A, B-pair concentration p(r) defined as

\[ p(r) = \text{average number of } A, B \text{ pairs, in the steady state, with } A \text{ and } B \text{ separated by a distance } r, \text{ per unit volume squared}. \]

The mutual diffusive flux of A’s and B’s to within some critical distance R of one another determines the rate of formation of C. Thus, we have

\[ \frac{df}{dt} = 4\pi R^2 D_0 \langle \delta \rho \rangle_R, \]

where all quantities on the right hand side of (1) are independent of time. The problem is to determine the form of the rate coefficient k in the circumstance that the reaction is diffusion controlled.

Because of the pairwise nature of the reaction, the important spatial dependence in this system can be accounted for through the A, B-pair concentration p(r) defined as

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\[ \frac{df}{dt} = 4\pi R^2 D_0 \langle \delta \rho \rangle_R, \]

where D_0 = D_A + D_B is the sum of the reactant diffusivities in the solvent under consideration. The pair concentration satisfies the steady state equation

\[ 0 = D_0 \nabla^2 p + \text{(reaction terms)}; \]

we assume, as in FD, that D_0 is independent of concentration. The reaction terms in (3) describe both losses and gains of A, B pairs. A given A, B pair of separation r can be lost due to reactive competition in two ways: the A can react with any other B, the B with any other A. The probability of losing a pair of separation r is then the probability of having such a pair to begin with (which is proportional to p(r)) multiplied by the sum of the probabilities of losing each of the members due to competition. The result is enhanced over the value predicted by simpler models which ignore competitive effects. Furthermore, it was demonstrated in FD that the enhancement, to first order, varied explicitly as the square root of the B species (called "sink" in FD) concentration, a result which differed from the concentration dependence elicited elsewhere by other techniques3,4 (see Ref. 14 of FD). As was pointed out in FD (Refs. 4, 6, 7, and 8), others have attempted to include correlations in their discussions of diffusion-controlled reactions. With this in mind, the readers of FD may be interested to note that a treatment of the same problem in terms of a Waite-type formalism5 leads to the same square root dependence in this system can be accounted for through the A, B-pair concentration p(r) defined as

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\[ \frac{df}{dt} = k_f A B f_A f_B, \]

where all quantities on the right hand side of (1) are independent of time. The problem is to determine the form of the rate coefficient k in the circumstance that the reaction is diffusion controlled.

Because of the pairwise nature of the reaction, the important spatial dependence in this system can be accounted for through the A, B-pair concentration p(r) defined as

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\[ \frac{df}{dt} = 4\pi R^2 D_0 \langle \delta \rho \rangle_R, \]

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\[ 0 = D_0 \nabla^2 p + \text{(reaction terms)}; \]

we assume, as in FD, that D_0 is independent of concentration. The reaction terms in (3) describe both losses and gains of A, B pairs. A given A, B pair of separation r can be lost due to reactive competition in two ways: the A can react with any other B, the B with any other A. The probability of losing a pair of separation r is then the probability of having such a pair to begin with (which is proportional to p(r)) multiplied by the sum of the probabilities of losing each of the members due to competition. Inasmuch as \(-k_f A B f_A f_B\) is the probable rate of loss, on the average, of any molecule of species i (i = A or B) in the sample, the terms in (3) describing competitive losses can be combined as the single ex-
pression \(-k(f_A + f_B)p\). In order to attain a steady production of C's, A's and B's must be replaced as the reaction evolves. Thus, (3) will contain gain terms reflecting this replacement. If the replacement is assumed to occur at random throughout the sample then \(p(r)\) is increased at the spatially uniform rate \(kf_A f_B (f_A + f_B)\). Defining the dimensionless pair concentration, \(u(r)\), by
\[
u(r) = 1 - p(r)/f_A f_B ,
\]
allows us to write (3) explicitly as
\[
0 = \nabla^2 u - \beta^2 u ;
\]
where \(\beta = k(f_A + f_B)/D_o^*\).

A solution to (5) subject to the boundary conditions \(u(\infty) = 0\)—implying that \(p\) approaches the sample-average pair concentration for large pair member separations—and \(u(R_0) = u(R) - 1\)—required by the radiation boundary condition on \(p\) at the reaction surface if \(R_o\) is the same parameter as in FD, Eq. (4.15)—is just
\[
u(r) = R^2 \left[ (1 + \beta R) (R + R_o + \beta RR_o)^{-1} \exp[-\beta(r - R)] \right] .
\]
When this solution is inserted into the right hand side of (3), and the result equated to the right hand side of (1) we find that \(k\) satisfies the nonlinear relation
\[
k = 4\pi D_o^* R \left[ (1 + \beta R) (R + R_o + \beta RR_o)^{-1} \right] .
\]
(7)

Now, we rewrite (7) in terms of the quantities defined in FD. Thus, we introduce \(\alpha = k(4\pi D_o^*)^{-1}\), \(\gamma = R \left[ (R + R_o)^{-1} \right]\), \(\tau = R \gamma^{-1}\), and \(\epsilon_i = (4\pi\gamma^{-1})^{1/2}\) for \(i = A\) or \(B\). Equation (7) can be rearranged, and, with these latter definitions, be recast as
\[
0 = \epsilon_i \left( R_o \gamma^{-1} \right) (\alpha \gamma^{-1})^3
- (1 + 2\tau \epsilon_i R_o \gamma^{-1}) (\alpha \gamma^{-1})^2
+ (2 + 2 \tau \epsilon_i) (\alpha \gamma^{-1}) - 1 ,
\]
(8)
where \(\epsilon_i = \epsilon_A^2 + \epsilon_B^2\). Since the parameters \(\epsilon_i\) are closely related to the volume fractions of the corresponding reactants, which, in turn, are presumed small, we see from (8) that \((\alpha \gamma^{-1}) - 1\). A perturbation expansion of \((\alpha \gamma^{-1})\) in successive powers of \(\epsilon\) leads to the result
\[
\alpha = \gamma \left[ 1 + (\epsilon_A^2 + \epsilon_B^2)^{1/2} + (\epsilon_B^2 + \epsilon_A^2) \left( \frac{1}{2} - \tau \right) + O(\epsilon) \right] .
\]
(9)

As pointed out in FD, the steady state bimolecular rate coefficient predicted by models which account for diffusion controlling but not for competitive effects is
\[
k_o = 4\pi D_o \gamma .
\]
Consequently, (9) shows that a Waite-type treatment of the reaction \(A + B \rightarrow C\) predicts an enhancement of the effective rate coefficient over \(k_o\) due to competition, which to first order is \((\epsilon_A^2 + \epsilon_B^2)^{1/2}\). The result obtained here is easily compared with Eq. (8.7) of FD. In the reaction we have discussed, the species A and B are treated on completely equal footing; (9) is symmetric in A and B. The reaction considered by FD, however, distinguishes between A and B. The B's are taken to be "indestructible"; they are not removed from the sample and are, therefore, not replaced. The analysis involved in obtaining (9) from (5) is all the same in this case except that \(\beta = k f_B D_o^*\) and \(\epsilon = \epsilon_B\). Thus, our (9) and Eq. (8.7) of FD agree that the dominant enhancement of the effective rate constant for the reaction \(A + B \rightarrow C\) is just \(\epsilon_B^2\). The two equations do, of course, disagree for higher order corrections, mirroring the approximations peculiar to the two different approaches. Whether an extremely precise experiment could uniquely discriminate between these two predictions seems to us problematical.

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3In addition to the references in FD see also D. Peak, H. L. Frisch, and J. W. Corbett, Radiat. Eff. 11, 149 (1971).
6For a discussion of the limitations of the Waite-type analysis see the review article by R. M. Noyes, Prog. React. Kinet. 1, 129 (1961); also see Ref. 4 of FD.
7We assume the A and B molecules interact through a central potential and that \(p(r)\) is spherically symmetric.