is adequately detected in measurements of NO_y will contribute significantly to the proper modeling of the phenomenon.

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Kinetics of Bimolecular Recombination Processes with Trapping

Jayendran C. Rasaiah,

Department of Chemistry, University of Maine, Orono, Maine 04469

Joseph B. Hubbard,*

Center for Chemical Engineering, Thermophysics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Robert J. Rubin,

Laboratory for Molecular Biology, National Institutes of Health (NIDDK), Bethesda, Maryland 20892

and Song Hi Lee

Department of Chemistry, Kyung Sung University, Pusan, Korea 608-023 *(Received: March 17, 1989; In Final Form: June 30, 1989)*

We report the results of a computer simulation and analysis of diffusion-controlled bimolecular recombination on a two-dimensional square lattice with the possibility of trapping. The following reactions are considered: (Ia) $A + A \rightarrow$ annihilation, (Ib) $A + T \rightarrow A_T$, (Ic) $A_T + A \rightarrow T$; (IIa) $A + A \rightarrow$ annihilation, (IIb) $A \rightarrow A_T$, (IIc) $A_T + A \rightarrow$ annihilation. Reaction I refers to recombination with bimolecular trapping (b), while reaction II refers to recombination with unimolecular trapping (b). In either case the time dependence of the trapped population (A_T) is described remarkably well by a mean field theory, while the free population (A) decays as a stretched exponential at long times ($\exp(-t^\alpha)$, $\alpha \sim {}^1/_2$). However, it is possible to distinguish between mechanisms I and II simply by monitoring a single particle density (A or A_T) for a range of initial conditions.

I. Introduction

Within the past few years there seems to have been a renaissance in the theory of diffusion-controlled chemical reactions. While earlier work was based on refinements of the enormously popular Smoluchowski concentration gradient theory or focused on the more formal aspects of the time evolution of an N-particle distribution function in some configuration space,[1-10] more recent developments have tended to emphasize the rather surprising and spectacular consequences of fluctuation-dominated kinetics; i.e., microscopic concentration fluctuations driven by random thermal fluctuations are magnified as the reaction progresses, so that an initially uniform system becomes macroscopically inhomogeneous and the concept of a reaction rate constant becomes invalid.[11-25] By a combination of analytic theories and computer simulations, it has been discovered that a large variety of simple reactions exhibit this anomaly; and in fact, one is hard put to come up with an example of a diffusion-controlled reaction in which fluctuations do not, in some time regime, play a major role. The two most carefully studied examples are[13-25]

$$A + B \rightarrow \text{annihilation} \tag{1.1a}$$

$$A + B \rightarrow B + C \tag{1.1b}$$

the first being an irreversible bimolecular recombination (or annihilation) while the second is irreversible catalysis (B is the catalyst which transforms A into C). Not surprisingly, the spatial dimensionality d (Euclidian or fractal) in which the reaction occurs is a key parameter, and there has been considerable emphasis on identifying the "upper critical dimension" d_c—the dimension at and above which fluctuations are not dominant and a mean field description is valid. Thus for reaction 1.1a $d_c = 4$, if the initial concentrations of A and B are equal, while for (1.1b) $d_c = \infty$ if the catalyst is immobile. Moreover, the long time decay kinetics

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is quite sensitive to initial concentrations. For instance, if $A(t)$ (the number density of A) and $B(t)$ are initially identical, then considering (1.1a) for large t[13,15,16]

$$A(t) \sim t^{-1} \qquad d \geq 4$$
$$A(t) \sim t^{-d/4} \qquad d \leq 4 \tag{1.2}$$

while if $A(0) < B(0)$

$$A(t) \sim \exp(-t) \qquad d \geq 3$$
$$A(t) \sim \exp(-t/\ln t) \qquad d = 2$$
$$A(t) \sim \exp(-t^{1/2}) \qquad d = 1 \tag{1.3}$$

at long times. For reaction 1.1b and a static random distribution of traps A, one has asymptotically[20-25]

$$A(t) \sim \exp(-t^{d/(d+2)}) \qquad 0 < d < \infty \tag{1.4}$$

What is typically observed in simulations is that a homogeneous kinetics description breaks down very fast in one dimension, retains its validity a good deal longer for $d = 2$, and except in the case of algebraic decay ($t^{-\alpha}$), one has to monitor the system for extremely long times before fluctuations begin to dominate in $d = 3$. $d = 2$ seems to be the ideal dimension in which to perform simulations inasmuch as topological complexity is present (particles can get around on another without reacting); the transition to fluctuation-controlled kinetics is rather unambiguous and does not require enormously long runs and an exact analytical description of the kinetics over the entire time domain is typically impossible, so that the outcome of the simulation is a genuine piece of experimental evidence and not simply the verification of some algorithm. Another reason to study reactions in two dimensions is that chemical reaction kinetics on surfaces is a subject of considerable practical importance.

An interesting variation of (1.1a) and (1.1b) is bimolecular recombination involving a single species (A), for which the Smoluchowski "target flux" description is not expected to hold.[1-10,14] In this instance one has

$$\mathrm{A} + \mathrm{A} \rightarrow \text{annihilation} \tag{1.5}$$

with

$$A(t) \sim t^{-d/2} \qquad d < 2$$
$$A(t) \sim t^{-1} \ln t \qquad d = 2$$
$$A(t) \sim t^{-1} \qquad d > 2 \tag{1.6}$$

The ln (t) correction is not an important feature in our study, so for all practical purposes we can take $d_c = 2$ for this reaction.[19]

Now imagine a reaction scheme that incorporates (1.1a), (1.1b), and (1.5) and suppose that the composite reaction takes place in two dimensions. An example would be

$$\mathrm{A} + \mathrm{A} \rightarrow \text{annihilation} \tag{1.7a}$$
$$\mathrm{A} + \mathrm{T} \rightarrow \mathrm{A_T} \tag{1.7b}$$
$$\mathrm{A_T} + \mathrm{A} \rightarrow \mathrm{T} \tag{1.7c}$$

where T refers to a stationary species, the members of which act as "traps" or immobilization sites for the diffusing A particles. Thus, (1.7a) refers to a bimolecular annihilation involving free A's, (1.7b) refers to bimolecular trapping, and (1.7c) represents an annihilation event involving a free A and a trapped A, with the subsequent regeneration of the trapping site. Physical realizations of this scheme include free-radical surface recombination in a heterogeneous (trapping) medium or even dimerization of macromolecules (enzymes or proteins) with the possibility of immobilization. Suppose, for the time being, that concentration fluctuations do not dominate the kinetics, that the various reactions involve only short-range encounters, and that the reactions are diffusion limited. Further, suppose that the initial condition consists of a uniform "quasi-random" distribution of A's and traps (T), with the constraint that no A initially occupies a trapping site (lattice terminology). By "quasi-random" we mean that each site not containing a trap is just as likely to contain an A as any other trap-empty site and that no site can be multiply occupied. At each time step each A moves one lattice spacing in a randomly chosen direction, their motions are completely uncorrelated, and an annihilation or trapping event occurs instantly whenever two (or more) A's occupy the same site simultaneously or whenever A jumps into a trap. Even without most of these stipulations we can immediately infer that

$$A(t) \sim t^{-1} \qquad \text{intermediate times} \tag{1.8a}$$
$$A(t) \sim \exp(-t) \qquad \text{long times} \tag{1.8b}$$

where (1.8a) reflects the "free A" recombination (1.7a) and (1.8b) indicates that, at sufficiently long times, the T and $\mathrm{A_T}$ populations are uniformly distributed and are nearly constant in time, so that the depleted A's are effectively diffusing in a homogeneous absorbing medium. An external "observer" monitoring $A(t)$ and aware of (1.7a) but not (1.7b) or (1.7c) would be forced to conclude (with considerable confusion) that the order of the reaction is indefinitely large, even though the kinetics is bimolecular. Also recall that, in the Smoluchowski picture ($d = 3$), the reactive flux into the target molecule is proportional to the sum of the diffusion coefficients of target and reactant species, which implies that immobilization (of the minority species, at least) will tend to impede the reaction. However, eq 1.8 predicts an acceleration of the reaction as time goes on and the mobile species is in the minority. Thus, we have a simple example in which a modification of the dynamics (by irreversible trapping) has a profound effect on chemical reaction kinetics.

Not surprisingly, a more scrupulous analysis leads to the conclusion that eq 1.8b is invalid at long times and that a "stretched" exponential decay is what actually occurs. Note that if the free A recombination mechanism is turned off by eliminating eq 1.7a, then as far as the A population is concerned, the long time behavior of $A(t)$ is described by the stretched exponential (1.4). This, then, implies that some features of reaction 1.7 will be dominated by concentration fluctuations while others should be more or less accurately described by a simple "mean field" theory (MFT), a theory in which, for instance, the position of each particle is randomized after each time step (perfect mixing). This idealization is particularly attractive, inasmuch as straightforward combinatorial reasoning gives the rate constants; these are inserted into the appropriate kinetic equations, and the concentrations of the various species can be obtained via numerical integration or mathematical analysis. One then makes a direct comparison with computer simulations or experiments for a wide range of initial concentrations. This procedure, which we follow in most of this study, enables us to address some of the more practical issues likely to be faced by kineticists worried about the range of validity of the equations they write down, as well as to probe some of the remarkable phenomena associated with the spontaneous breakdown of macroscopic spatial homogeneity.

Another important feature of this study is a detailed comparison of "bimolecular" vs "unimolecular" trapping. Consider the reaction scheme

$$\mathrm{A} + \mathrm{A} \rightarrow \text{annihilation} \tag{1.9a}$$
$$\mathrm{A} \rightarrow \mathrm{A_T} \tag{1.9b}$$
$$\mathrm{A} + \mathrm{A_T} \rightarrow \text{annihilation} \tag{1.9c}$$

and compare this with reaction 1.7. In (1.7) the trapping sites T are randomly distributed and are "immortal" by eq 1.7c. In eq 1.9b, however, immobilization occurs at a certain rate or frequency which is independent of particle location, and so reaction 1.9c simply annihilates a free A along with a trapped A without producing a stationary trap as in eq 1.7c. A physical realization of this unimolecular trapping is one in which the rate-determining mechanism is a random, temporal fluctuation in the internal state of a free A. Therefore, by studying both reaction schemes (1.7) and (1.9), one can compare the chemical effects of topological vs temporal randomness in the trapping mechanism.

This paper is organized as follows. In section II we discuss simulation details for free annihilation and introduce the mean

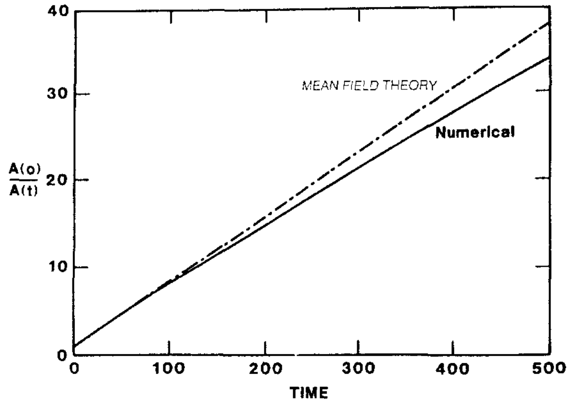

Figure 1. Simulation (numerical) results for A + A → annihilation are compared with MFT (eq 2.4) with $k = {}^3/_4$ and $A(0) = 0.1$. Exact agreement is observed at short times while at longer times the departure from $k = {}^3/_4$ is obvious. In either case $A(t) \sim t^{-1}$ for long times. Note that the evolution of correlations suppresses the reaction rate relative to MFT.

field kinetic equations, along with their solutions for annihilation with traps. Section III discusses the simulation of annihilation reactions on a surface in the presence of traps and compares the results of various "hopping" algorithms. It provides an in-depth comparison of the consequences of unimolecular vs bimolecular trapping, as well as a comparison of simulation results with MFT. In the latter part of this section we present evidence for the breakdown of MFT and discuss a theoretical model which might help to account for this behavior. Our results are discussed in section IV. The Appendix contains the mathematical details of our MFT/combinatorial derivation of the reaction rate constants.

II. Free Annihilation and the Mean Field Kinetic Equations for Annihilation with Traps

We first consider annihilation reactions in the absence of traps. For example, the reaction

$$\text{A} + \text{A} \rightarrow \text{annihilation} \tag{2.1}$$

is expected, assuming mean field behavior, to follow second-order kinetics

$$\mathrm{d}A(t)/\mathrm{d}t = -kA(t)^2 \tag{2.2}$$

in which the concentration $A(t)$ of A changes with time according to the relation

$$A(0)/A(t) = 1 + A(0)kt \tag{2.3}$$

We have studied a simple model for this reaction by computer simulation of a two-dimensional square lattice with 10 000 sites and periodic boundary conditions in which each lattice site is free or occupied by a particle. In the simulation every particle is moved in each time step along one of four directions with a probability of $^1/_4$; simultaneous occupancy of a lattice site leads to annihilation by pairs. Since all of the free particles are moved in each time step, two free particles on adjacent sites cannot annihilate each other. In a variation of this procedure we can also restrain a particle from moving by introducing a "staying probability" p_s; the probability of moving in any one of the four directions around a site at each time step is then equal to $(1 - p_s)/4$. Now the annihilation of two adjacent particles, one free and the other immobilized, is possible.

A combinatorial analysis (which assumes equal probability of occupation for all sites) leads to the rate equation (see Appendix)

$$\mathrm{d}A(t)/\mathrm{d}t = -(3/4)A(t)^2 + (1/4)A(t)^3 - (1/32)A(t)^4 \tag{2.4a}$$

when the staying probability p_s is zero. This implies a rate constant k for free particle annihilation equal to $^3/_4$ when only binary collisions are important. The computer simulations with $A(0) = 0.1$ (Figure 1), averaged over 1000 initial configurations, agree with the calculated k at short times but also show that the apparent rate constant k is less than $^3/_4$ for long times. This implies that the evolution of correlations as the reaction proceeds affects the rate constant at long times. Figure 2 shows snapshots of the reaction on a smaller lattice (50 × 50) at the beginning ($t = 0$) and after 10 time steps ($t = 10$) for the case where half the lattice sites are occupied at the start ($A(0) = 0.5$). Prominent vacancies or holes are seen even after 10 time steps. In Figure 3 we have the corresponding results for the concentration of $A(t)$ as a function of time for different staying probabilities p_s. It appears that a small increase in p_s from zero increases the concentration of free A's, while a further enhancement of p_s decreases the population of free particles below what is expected at a staying probability of zero. This crossover in the free particle concentration appears to take place at a critical staying probability $p_s^c = {}^1/_5$ for a square lattice which is the theoretical prediction based on a combinatorial analysis (see Appendix). The analysis, which assumes a uniform distribution of A's, provides a relationship between the free particle rate constant k and the staying probability p. For a square lattice

$$k = 3/4 + p_s/2 - (5/4)p_s^2 \tag{2.4b}$$

from which it is seen that k has a maximum at $p_s = {}^1/_5$ and k is zero at p_s equal to unity.

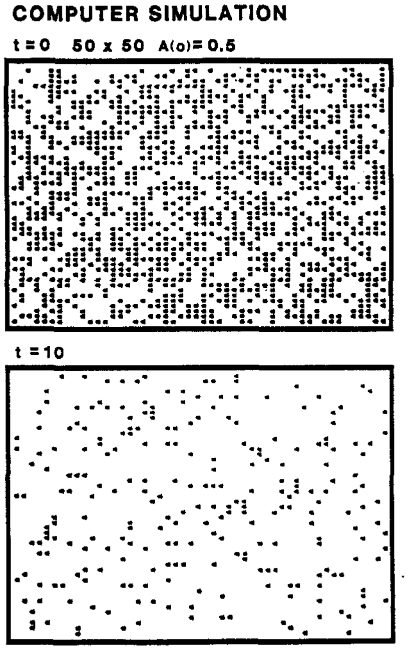

Figure 2. A snapshot of the reaction A + A → annihilation on a square lattice containing 2500 sites and 1250 particles initially. At each time step each particle executes a jump to a randomly chosen nearest-neighbor lattice site (with equal probability), and pair annihilation occurs instantly whenever two or more A's occupy the same site simultaneously. Periodic boundary conditions are imposed.

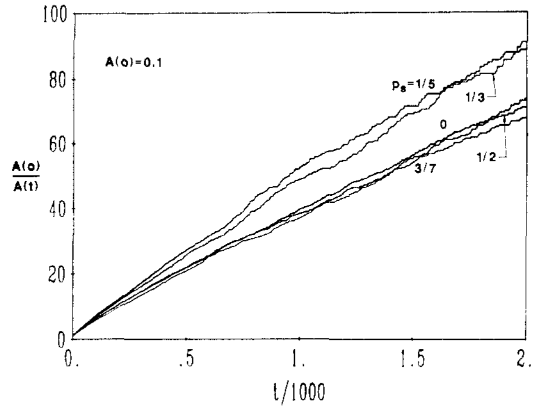

Figure 3. Simulation results for bimolecular recombination without trapping for various "staying probabilities" p_s, with $0 \leq p_s \leq {}^1/_2$. Note that $A(t)$ decays fastest for $p_s = {}^1/_5$. p_s not equal to zero allows a pair of nearest-neighbor A's to recombine.

A finite staying probability implies a fleeting immobilization of a particle, and it is natural to extend this idea further and enquire how the concentration of free A's is affected by permanent immobilization in traps. We consider two possibilities, bimolecular and unimolecular trapping, as discussed in the Introduction, where (a) traps of density $T(0)$ are distributed randomly over the lattice sites or where (b) there are no traps at the beginning but the free particles become trapped or immobilized in each time step with a probability k'. In either case a trapped particle is annihilated with a rate constant k_T when a free particle moves in on it; this is also the rate at which particles are trapped in the bimolecular trapping reactions. For unimolecular trapping, the annihilation of a free A and a trapped A produces a vacant lattice site, while the same reaction in bimolecular trapping restores a vacant trap at the lattice site. The process by which trapped A's are produced in the bimolecular and unimolecular reactions inevitably leads to a finite concentration of trapped A's at long times where the prospect of further annihilation vanishes along with the free A concentration.

The computer simulations of bimolecular and unimolecular trapping/annihilation reactions are discussed in section III. The analysis of the results makes explicit use of the mean field kinetic rate equations which we will now consider.

(*a*) *Bimolecular Trapping Reactions.* We have the reactions

$$\mathrm{A} + \mathrm{A} \xrightarrow{k} \text{annihilation} \tag{2.5}$$

$$\mathrm{A} + \mathrm{T} \xrightarrow{k_T} \mathrm{A_T} \tag{2.6}$$

$$\mathrm{A_T} + \mathrm{A} \xrightarrow{k_T} \mathrm{T} \tag{2.7}$$

where $A(t)$ and $A_T(t)$ are the densities (or concentrations) of free particles and trapped particles, respectively, at time t, and $T(t)$ is the density of empty traps. Since the total density of traps (empty and filled) is conserved

$$T(0) = T(t) + A_T(t) \tag{2.8}$$

The mean field kinetic equations are

$$\begin{aligned} \mathrm{d}A(t)/\mathrm{d}t &= -kA(t)^2 - k_T A(t)\, T(t) - k_T A(t)\, A_T(t) \\ &= -A(t)[kA(t) + k_T T(0)] \end{aligned} \tag{2.9}$$

$$\mathrm{d}T(t)/\mathrm{d}t = -\mathrm{d}A_T(t)/\mathrm{d}t = -k_T A(t)[T(t) - A_T(t)] \tag{2.10}$$

Integrating eq 2.10 and making use of (2.8), one finds that

$$A_T(t) = (T(0)/2)[1 - \exp(-2k_T I(t))] \tag{2.11}$$

where

$$I(t) = \int_0^t A(t')\,\mathrm{d}t' \tag{2.12}$$

It follows from eq 2.11 that $T(0)/2$ is an upper bound for $A_T(\infty)$; that is to say, no more than *half the number of traps can be filled at the end of the bimolecular recombination reaction with trapping.* Integration of eq 2.9 leads to

$$\frac{A(t)}{A(0)} = \frac{e^{-k_T T(0)t}}{1 + K(1 - e^{-k_T T(0)t})} \tag{2.13}$$

where

$$K = a/b \tag{2.14}$$

in which

$$b = k_T/k \tag{2.15}$$

is the ratio of the rate constants for free and trapped particle annihilations and

$$a = A(0)/T(0) \tag{2.16}$$

is the ratio of the concentrations of free particles to traps at the beginning. On substituting eq 2.13 in eq 2.12 and integrating, it is found that

$$I(t) = (1/k)\ln\,[1 + K(1 - \exp(-k_T T(0))t] \tag{2.17}$$

Using this in eq 2.11 it follows that

$$A_T(t) = \frac{T(0)}{2}\left\{1 - \left(\frac{1}{1 + K(1 - e^{-k_T T(0)t})}\right)^{2b}\right\} \tag{2.18}$$

As $t \rightarrow \infty$

$$A_T(\infty) = \frac{T(0)}{2}\left\{1 - \frac{1}{(1 + K)^{2b}}\right\} \tag{2.19}$$

If $K \gg 1$ or $a \gg 1$, $A_T(\infty) \rightarrow T(0)/2$. Defining the total density of A's, $A_{\mathrm{Tot}}(t) = A(t) + A_T(t)$, we have from eq 2.13 and 2.18 that $A_{\mathrm{Tot}}(\infty) = A_T(\infty)$ since the number of free particles is zero at infinitely large times.

In the limit when the free particle annihilation is turned off (i.e., $k = 0$), K is zero, b is infinite, and $A(t)$ decays exponentially with time (see eq 2.13):

$$A(t) = A(0)\exp(-k_T T(0)t) \quad (k = 0) \tag{2.20}$$

Integrating $A(t)$ with respect to time (or upon expanding the logarithm in eq 2.17), it is found that

$$I(t) = (a/k_T)(1 - \exp(-k_T T(0)t) \quad (k = 0) \tag{2.21}$$

Inserting this in eq 2.11, we obtain an expression for the number of particles trapped at time t when there is no free particle annihilation:

$$A_T(t) = (T(0)/2)[1 - \exp\{-2a(1 - e^{-k_T T(0)t})\}] \tag{2.22}$$

At infinitely large times ($t \rightarrow \infty$), this reduces to

$$A_T(\infty) = (T(0)/2)\{1 - e^{-2a}\} \tag{2.23}$$

Equations 2.22 and 2.23 agree with the $K = 0$ and $b = \infty$ limit of eq 2.18 and 2.19, respectively.

(*b*) *Unimolecular Trapping Reactions.* For this case we have the series of reactions

$$\mathrm{A} + \mathrm{A} \xrightarrow{k} \text{annihilation} \tag{2.24}$$

$$\mathrm{A} \xrightarrow{k'} \mathrm{A_T} \tag{2.25}$$

$$\mathrm{A_T} + \mathrm{A} \xrightarrow{k_T} \text{annihilation} \tag{2.26}$$

The rate equations are

$$\mathrm{d}A(t)/\mathrm{d}t = -A(t)[kA(t) + k' + k_T A_T(t)] \tag{2.27}$$

$$\mathrm{d}A_T(t)/\mathrm{d}t = A(t)[k' - k_T A_T(t)] \tag{2.28}$$

On integrating eq 2.28, we have

$$A_T(t) = (k'/k_T)[1 - \exp(-k_T I(t))] \tag{2.29a}$$

where $I(t)$ is given by eq 2.12. Note the similarity of eq 2.29 to eq 2.11. Since the integral $I(\infty)$ is positive, it follows that k'/k_T is an upper bound for $A_T(\infty)$. Substituting eq 2.29 in eq 2.27, one obtains

$$\mathrm{d}A/\mathrm{d}t = -A(t)[kA(t) + 2k' - k'\exp(-k_T I(t))] \tag{2.29b}$$

where $I(t)$ is defined by eq 2.12. It can be verified by direct substitution that integration of the second-order differential equation leads to[26]

$$A(t) = -2\frac{k'}{k} + \frac{k'}{k - k_T}\exp(-k_T I(t)) + C\exp(-kI(t)) \tag{2.30}$$

where

$$C = A(0) + 2k'/k - k'/(k - k_T) \tag{2.31}$$

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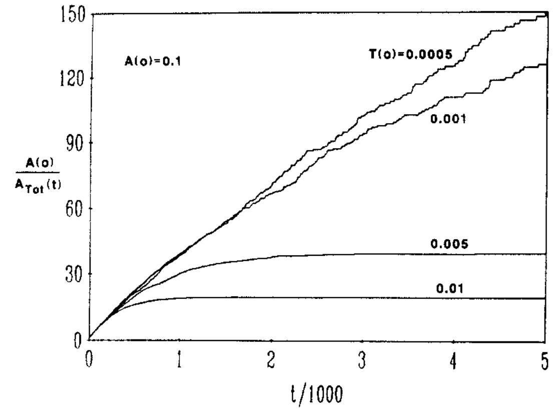

Figure 4. Simulation results for recombination plus bimolecular trapping on a 100 × 100 square lattice initially containing 1000 particles and various numbers of randomly distributed traps T. Note the rapid approach to a steady state with increasing trap density. A_{Tot} is given by $A(t) + A_T(t)$. The staying probability $p_s = 0$.

At infinite time ($t = \infty$), the number of free particles is zero, i.e., $A(\infty) = 0$, and it follows that when $k \neq k_T$ (i.e., $b \neq 1$)

$$-2 + [1/(1-b)]Y + [A(0)k/k' + 2 - 1/(1-b)]Y^{1/b} = 0 \qquad (2.32)$$

where

$$Y = \exp(-k_T I(\infty)) \qquad (2.33)$$

is the root of the transcendental eq 2.32. Note that Y is a function of $A(0)k/k'$ and b. When $t \to \infty$, eq 2.29 implies that

$$A_T(\infty)/k' = (1/k_T)(1 - Y) \qquad (2.34)$$

and Y must therefore lie between 0 and 1, since $A_T(\infty)$ and k' are positive. It follows from eq 2.34 that *MFT predicts that k'/k_T is an upper bound for $A_T(\infty)$ in unimolecular trapping/reactions.* Equations 2.32 and 2.34 can be used to determine Y and $A_T(\infty)/k'$, respectively, provided k and k_T are known and $b = k_T/k \neq 0$ or 1.

In the limit when $k = 0$ ($b = \infty$), i.e., when there is no free particle annihilation

$$A(t) = A(0) - 2k'I(t) - (k'/k_T)[\exp(-k_T I(t)) - 1] \qquad (2.35)$$

in which the integral $I(t)$ appears. As $t \to \infty$, $A(t) \to 0$ and it follows that

$$A(0) = 2k'I(\infty) + (k'/k_T)[\exp(-k_T I(\infty)) - 1] \qquad (2.36)$$

i.e., $Y = \exp(-k_T I(\infty))$ is the root of

$$[k_T A(0)/k' + 1] + 2 \ln Y - Y = 0 \qquad (2.37)$$

We use eq 2.37 and 2.34 to determine Y and $A_T(\infty)/k'$ when $k = 0$ assuming k_T is known.

The mean field kinetic equations, which are independent of the dimensionality, say nothing about the magnitudes of the rate constants; for this a more detailed description of the kinetic encounters is required when it is found that the free particle rate constant is determined by the dimensionality and symmetry of the lattice as well as the coordination number of the sites. We have already referred to the calculation of k for free particle annihilation using a combinatorial argument which leads to $k = {}^3/_4$ when the staying probability p_s is zero; the details of this argument are given in the Appendix. The argument is unchanged in the presence of traps in bimolecular reactions leading to the same value of k. Moreover, the rate constant k_T for annihilation between a free particle and one that is trapped in a bimolecular recombination is easily calculated. Since there are four sites around a trap and the probability of moving a free particle in each of the four directions is ${}^1/_4$ when the staying probability is zero, it follows that $k_T = 1$ assuming a uniform distribution of traps and particles and a zero staying probability. At long times we expect again that $k_T = 1$ on the assumption that the trapped particles are uniformly distributed over the traps; thus $b = {}^4/_3$ for short times and possibly also for long times.

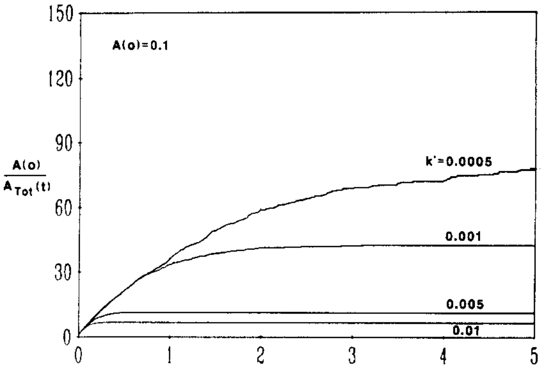

Figure 5. The same situation as in Figure 4, except that trapping is unimolecular with a rate constant k'.

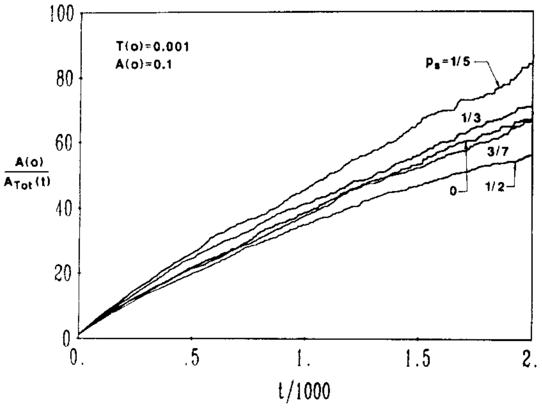

Figure 6. Simulation results for recombination plus bimolecular trapping for various "staying probabilities" p_s. A_{Tot} is given by $A + A_T$.

III. Simulation of Bimolecular and Unimolecular Trapping/Annihilation Reactions: Comparison with Mean Field Theory

The simulations of bimolecular trapping/annihilation reactions were carried out in much the same way as the simulations of free annihilation on a 2-d lattice except that we started with random distributions of free traps of density $T(0)$ and free particles of density $A(0)$. The concentration of free particles $A(t)$ and trapped particles $A_T(t)$ were recorded as a function of time t during a run, and ensemble averages were calculated over 100 or so initial configurations of traps and particles for a set of initial conditions defined by the trap density $T(0)$ and the free particle density $A(0)$. The trap density $T(0)$ ranged from 0.0005 to 0.5 while the initial free particle density $A(0)$ lay between 0.1 and 0.5. Figure 4 shows that a steady-state concentration of $A_{Tot}(t)$ is approached rapidly with increasing trap density. The simulations for unimolecular trapping reactions were carried out analogously. In this case, there are no traps initially but free particles were immobilized with a probability k' in each time step. The results were recorded and averaged in the same way as the runs for bimolecular trapping/annihilations, with k' replacing $T(0)$ as the distinguishing trapping parameter, k' ranged between 0.0005 and 0.5, and the initial free particle densities $A(0)$ were between 0.1 and 0.5. Steady-state concentrations of trapped particles were reached more rapidly with increasing probabilities k' of particle immobilization; see Figure 5. The effects of different staying probabilities on the total densities of free and trapped particles as a function of time are illustrated in Figures 6 and 7. The simulation of free particle annihilation is compared in Figure 8 with those of uni- and bimolecular trapping/annihilations when the trapping rate k' is equal to the initial trap density $T(0)$. The initial particle density $A(0)$ is the same in all three simulations, and the staying probability is zero. It appears that the unimolecular trapping scheme reaches a steady state, as measured by $A_{Tot}(t)$, much

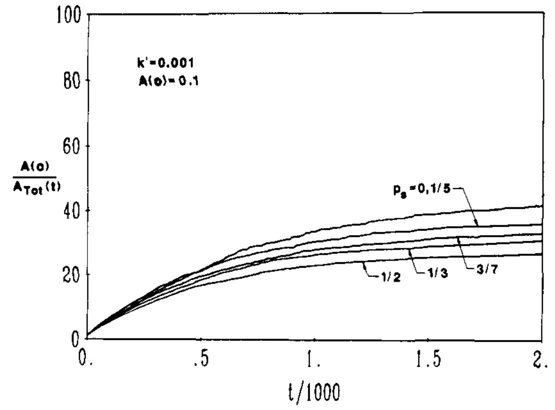

Figure 7. Simulation results for recombination plus unimolecular trapping for various values of p_s.

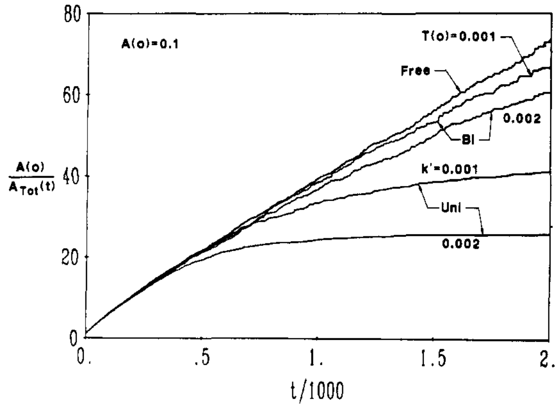

Figure 8. Simulation results comparing uni- to bimolecular trapping (plus recombination), where the initial trap density $T(0)$ is equal to the trapping rate k'. "Free" refers to recombination without trapping. The staying probability $p_s = 0$.

TABLE I: Ratio $A_T(\infty)/T(0)$ as a Function of the Ratio of the Initial Number of Free Particles to Traps $A(0)/T(0) = a$ in a Recombination Reaction with Bimolecular Trapping When the Staying Probability $p_s = 0$; Comparison of Computer Simulation with the Predictions of MFT

	$A_T(\infty)/T(0)$				
	eq 2.19[a]				
$A(0)/T(0)$	$b = \infty$	$b = 4/3$	$b = 1.0$	$b = 0.5$	simulation
0.1	0.091	0.088	0.086	0.083	
0.1429	0.124	0.119	0.117	0.111	
0.2	0.165	0.155	0.152	0.143	0.154
0.4	0.275	0.251	0.245	0.222	0.252
0.5	0.316	0.286	0.278	0.250	0.288
0.6	0.349	0.314	0.305	0.273	0.316
1.0	0.432	0.388	0.375	0.333	0.394
1.25	0.459	0.414	0.401	0.357	0.414
1.667	0.482	0.442	0.429	0.389	0.442
2.5	0.496	0.470	0.459	0.417	0.466
5.0	0.5	0.492	0.486	0.454	0.490
7.0	0.5	0.496	0.492	0.466	0.487
10.0	0.5	0.498	0.496	0.476	0.508

[a] In eq 2.19, $b = k_T/k$ and $K = a/b$ where $a = A(0)/T(0)$. For a random distribution of traps and free A's, a combinatorial analysis shows that $k = 3/4$ and $k_T = 1.0$ when the staying probability $p_s = 0$.

TABLE II: Ratio $A_T(\infty)/k'$ as a Function of $A(0)/k'$ for Recombination Reactions with Unimolecular Trapping When the Staying Probability $p_s = 0$; Comparison of Computer Simulation with Predictions of MFT[a]

	$A_T(\infty)/k'$			
	eq 2.34[a]			
$A(0)/k'$	$b = \infty$	$b = 4/3$	$b = 0.5$	simulation
0.1	0.096	0.088	0.093	
0.2	0.186	0.159	0.175	0.17
0.4	0.350	0.267	0.312	0.31
0.5	0.424	0.309	0.371	0.371
0.6	0.494	0.346	0.424	0.423
1.0	0.744	0.461	0.600	0.589
1.25	1.88	0.513	0.688	0.635
1.67	1.07	0.580	0.809	0.696
2.5	1.38	0.671	0.989	0.807
5.0	1.94	0.802	1.30	0.975
7.0	2.19	0.852	1.45	1.34
10.0	2.41	0.894	1.60	1.46
20.0	2.62	0.949	1.85	1.75
100.0	2.66	0.992	2.26	2.35
200.0	2.66	0.997	2.38	2.58
250.0	2.66	0.998	2.41	2.67
300.0	2.66	0.998	2.43	2.68

[a] For $b \neq \infty$, Y is obtained as the solution to eq 2.32 assuming $k = 3/4$ and $k_T = 1$ ($b = 4/3$) or $k_T = 0.375$ ($b = 0.5$). For $b = \infty$ ($k = 0$), Y is the solution of eq 2.37 assuming $k_T = 0.375$.

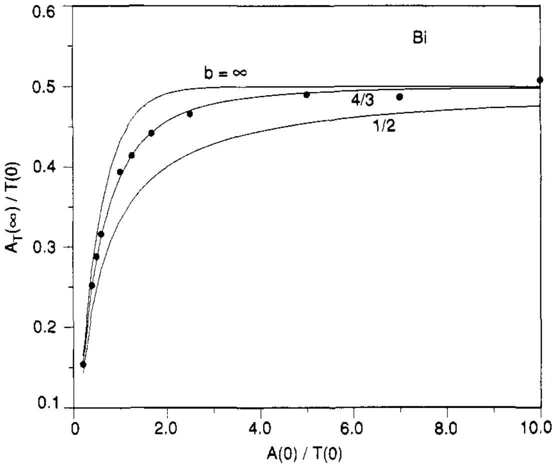

Figure 9. Simulation results (●) for the normalized infinite time "yield" $A_T(\infty)/T(0)$ are compared with mean field theory (MFT) for recombination plus bimolecular trapping. b is given by k_T/k, where k_T is the trapping rate and k is the bimolecular annihilation rate. $b = 4/3$ corresponds to "perfect mixing" or "ideal" MFT.

sooner than the bimolecular recombination with trapping. However, this is misleading since $A_{Tot}(t)$ is the total density of particles, both free and trapped, and a plateau in Figure 8 implies that it is the sum of these two densities rather than the number of trapped particles that has quickly reached a constant for unimolecular trapping. In the rest of this paper we will take care to distinguish between these two densities and find that the concentration of trapped particles $A_T(t)$ fluctuates over a longer time before reaching a limit for unimolecular than for bimolecular trapping reactions. The trapped particle densities at infinite time $A_T(\infty)$ determined by computer simulation are summarized in the last columns of Tables I and II for both types of recombination reactions with trapping.

The simulation data as a function of time, over the course of many runs for several initial sets of conditions, were found at first to be too numerous and too complicated to analyze since neither the rate equations nor the rate constants were known. Although it was tempting to compare the data with the mean field kinetic equations, this still left open the choice of rate constants k and k_T for uni- and bimolecular trapping reactions. Examination of the simulations for the bimolecular trapping/annihilations showed that $A_T(\infty)/T(0)$ was a function only of the initial ratio ($A(0)/T(0)$) of free particles to traps (see last column of Table I). Mean field theory (MFT), eq 2.19, predicts that this is determined by the ratio $b = k_T/k$ of the rate constants k_T and k for trapped particle and free particle annihilations, respectively, thereby providing a simple test of the theory for assumed values of b; see Table I and Figure 9. Likewise, an analysis of the results for unimolecular trapping was carried out by recording $A_T(\infty)/k'$ as a function of $A_T(0)/k'$ (last column of Table II). Results of the simulations of $A_T(\infty)/k'$ are summarized in Table II along with

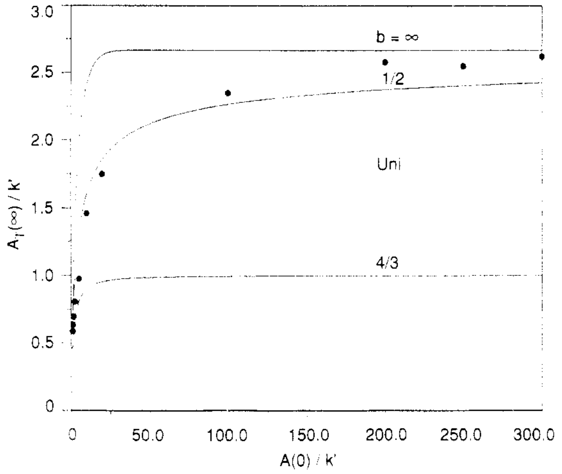

Figure 10. Simulation results (●) for the normalized infinite time "yield" $A_T(\infty)/k'$ are compared with mean field theory (MFT) for recombination plus unimolecular trapping. b is the same as in Figure 9. Note that $b = {}^4/_3$ gives a poor estimate of the yield for large values of $A_T(0)/k'$.

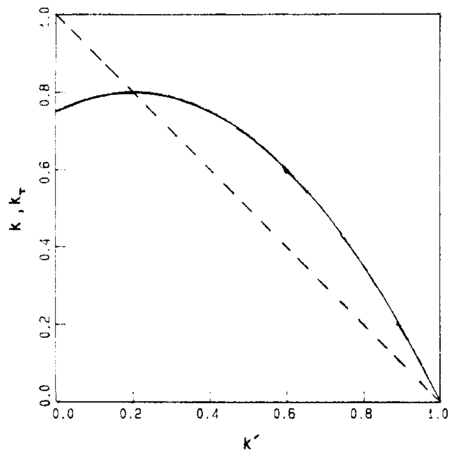

Figure 11. Plots of the rate constants k and k_T for free and trapped particle annihilations, respectively, as a function of k' for unimolecular recombination plus trapping; see eq 3.1 and 3.2. The same plots convey the dependence of k and k_T on the staying probability p_s of free particles in bimolecular recombination plus trapping reactions. $k' = {}^1/_5$ is the dividing line between $b > 1.0$ and $b < 1.0$, where $b = k_T/k$.

TABLE III: Ratio $A_T(\infty)/k'$ as a Function of $A(0)/k'$ for Recombination Reactions with Unimolecular Trapping When the Staying Probability $p_s = 0$; Comparison of Computer Simulation with Predictions of MFT and Combinatorial Analysis of Rate Constants

			$A_T(\infty)/k'$	
$A(0)/k'$	k'	b	calcd[a]	simulation
0.1	0.5	0.727	0.092	
0.2	0.5	0.727	0.172	0.17
0.4	0.5	0.727	0.304	0.31
0.5	0.5	0.727	0.360	0.371
0.6	0.5	0.727	0.410	0.423
1.0	0.5	0.727	0.574	0.589
1.25	0.4	0.8	0.612	0.635
1.67	0.3	0.888	0.665	0.696
2.5	0.2	1.000	0.739[b]	0.807
5.0	0.1	1.142	0.850	0.975
7.0	0.0143	1.302	0.860	1.34
10.0	0.01	1.311	0.900	1.46
20.0	0.005	1.322	0.953	1.75
100.0	0.001	1.333	0.992	2.35
200.0	0.0005	1.333	0.996	2.58
250.0	0.0004	1.333	0.998	2.67
300.0	0.00033	1.333	0.998	2.68

[a] Calculated from eq 2.34 in which Y is obtained as the solution to eq 2.32 assuming $k_T = 1 - k'$, $k = 3/4 + k'/2 - (5/4)k'^2$, and $b = k_T/k = 4/(3 + 5k')$. [b] From the numerical solution of the differrential equations (2.27) and (2.28).

MFT calculations assuming $b = 0.5$, ${}^4/_3$, and ∞. Figure 10 compares the MFT calculations of $A_T(\infty)/k'$ as a function $A_T(0)/k'$ with the computer results. An infinite b corresponds to the assumption of an extremely large rate constant k_T for trapped particle annihilation or a near-zero rate constant k for free particle annihilation. The simulations are compared with the predictions of eq 2.34 and 2.32 for finite values of b or eq 2.34 and 2.37 for $b = \infty$ which are the predictions of mean field theory.

We are now in a position to make a detailed comparison of our simulations with the predictions of mean field theory. The assumption that $k = {}^3/_4$ and $k_T = 1.0$ (i.e., $b = {}^4/_3$) leads to mean field kinetic equations that are in excellent agreement with the computer simulations of the number of trapped particles at infinite time in bimolecular trapping/annihilation reactions (see Table I and Figure 9) but less so for unimolecular trapping reactions. The disagreement in the second case could be due to the wrong choice of the rate constants k and k_T rather than the incorrectness of MFT. Moreover, assuming mean field behavior, k_T can be estimated for unimolecular trapping/annihilation reactions by noting that in eq 2.34 $Y \to 0$ as $A(0)/k'$ becomes large; the rate constant k_T must therefore be equal to the asymptotic value of $k'/A_T(\infty)$ as $A(0)/k'$ increases. From Figure 10 we find that k_T is approximately 0.375 rather than unity for large $A(0)/k'$ (i.e., small k' at finite $A(0)$)! Retaining $k = {}^3/_4$ as the rate constant for free annihilation we surmise that $b = 0.5$ in this regime. However, this argument ignores the coupling between the rate constants k and k_T through the spontaneous generation of trapped particles with probability k', so that the annihilations of free and trapped particles become correlated. An analysis of this, under certain assumptions, will be considered next.

The correlation between the densities of free and trapped A's in unimolecular reactions is easily calculated if they are assumed to be randomly distributed, since k now takes on the role of a finite staying probability p_s which not only immobilizes a free A but transforms it simultaneously into a trapped particle A_T. From the combinatorial arguments presented in the Appendix it follows, mutatis mutandis, that

$$k = 3/4 + k'/2 - (5/4)k'^2 \tag{3.1}$$

and

$$k_T = 1 - k' \tag{3.2}$$

Figure 11 shows plots of k and k_T as functions of k'. Note that the rate constants k and k_T are zero for k' equal to unity, while the curves of k and k_T intersect at the maximum value of k which occurs at $k' = {}^1/_5$. Eliminating k' between eq 3.1 and 3.2, we arrive at a quadratic equation for k_T

$$5k_T^2 - 8k_T + 4k = 0 \tag{3.3}$$

which has only one physically acceptable solution

$$k_T = [4 - 4(1 - 5k/4)^{1/2}]/5 \tag{3.4}$$

For small k

$$b = k_T/k \sim 0.5 \tag{3.5}$$

More generally, we find from eq 3.3 and 3.2 that

$$b = 4/(3 + 5k') \tag{3.6}$$

which implies that $b \sim 0.5$ only if k' is close to unity. All of our assumed values of k' are however less than or equal to 0.5; see Table III.

Before continuing this discussion of unimolecular trapping and recombination, we note that if we substitute p_s for k' in the above equations we will be considering the dependence of k and k_T on the staying probability p_s for bimolecular/trapping plus recombination reactions. Figure 11 and the discussion presented above may also be viewed in this light. That is to say, bimolecular trapping and recombination with a finite staying probability is related to the corresponding unimolecular reaction with zero

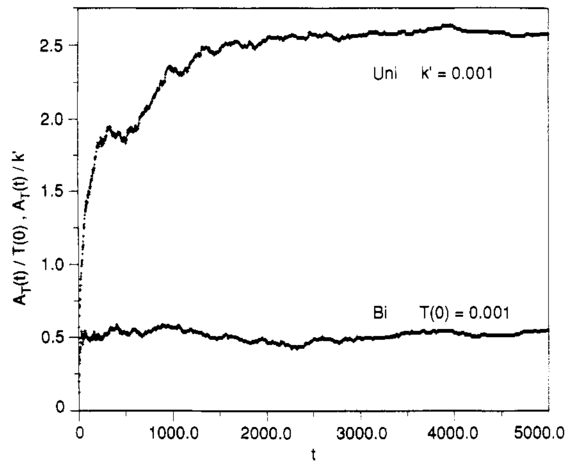

Figure 12. Simulation results of normalized trapped particle densities for both bimolecular ($A_T(t)/T(0)$) and unimolecular ($A_T(t)/k'$) trapping (plus recombination) are plotted vs time. Note that, for identical values of the initial trap density and trapping rate, the stationary state is attained more slowly for unimolecular than for bimolecular trapping.

staying probability, provided the free and trapped A's are uniformly distributed.

Returning to unimolecular trapping/annihilations it appears, from Figure 10 and Table II, that mean field theory with $b = 0.5$ and the coupling between k and k_T ignored provides an accurate prediction of the simulations of $A_T(\infty)/k'$ for small values of $A(0)/k'$ (between 0.1 and 0.6) but is less satisfactory at the high end of $A(0)/k'$. In this limit, a value of $b = \infty$ gives answers that are closer to the simulated values of $A_T(\infty)/k'$; the crossover in behavior seems to occur around $A(0)/k'$ equal to unity. Nevertheless, the assumption of $b = 0.5$ gives the best overall fit to the simulation data (see Table II). However, we regard this as accidental, since it ignores the coupling between the free and trapped particle annihilations and provides no explanation of the empirically determined rate constant $k_T = 0.375$ for the annihilation of trapped A's when $A(0)/k'$ is large (i.e., when k' is relatively small). When the coupling between the two rate constants k and k_T is taken into account, b is found to vary with k', as shown in eq 3.6, and we arrive at the results summarized in Table III. Here the predictions of MFT are calculated assuming that k and k_T are given by eq 3.1 and 3.2, respectively. Note that $A_T(\infty)/k'$ is now a function not only of $A_T(0)/k'$ but also of k' as well. The agreement between the simulations and theory is excellent at the low end of $A(0)/k'$ but not when k' is small and $A(0)/k'$ is large. At this end k_T is expected to be 0.375 rather than $1 - k' \sim 1$ according to the theory. The reason for this discrepancy may lie in the assumptions underlying our combinatorial calculations, which take into account the correlation between free and trapped A's but ignore the correlation between trapped A's. The trapped A's could shield one another from annihilation by free particles, but the combinatorial calculation ignores the effect of this on the annihilation rates. These difficulties imply that the correlations which may develop among the different species in unimolecular trapping/recombination reactions are much more complex than what might be deduced from a random mixing of free and trapped particles. Instead of a random distribution of trapped A's, one might have, for instance, a more or less random distribution of clusters of trapped particles which scale the rate constants so that the kinetic mean field equations are still obeyed for trapped A's at infinite time. The calculation of the rate constants, within the framework of the MFT, as a function of the initial conditions now becomes a much more difficult task. Another possibility is that MFT breaks down at large times for small values of rate constant k', when the annihilation of a few trapped A's by fewer free particles could become diffusion controlled, with the rate constant k_T for trapped particle annihilation determined by the relevant diffusion coefficient.

So far our analysis has dealt with the end product of the reactions, i.e., the numbers of trapped particles at infinite time and their dependence primarily on the initial conditions. We will now discuss the changes in free and trapped particle densities during the course of these reactions. In Figures 12 and 13 the simulations of bimolecular and unimolecular trapping/annihilation reactions are compared with each other over 1000 or more time steps for the same values of $T(0)$ and k'. When $T(0) = k' = 0.005$ the limiting value of $A_T(t)/T(0)$ for a bimolecular reaction is reached much sooner than the corresponding limit of $A_T(t)/k'$ for a unimolecular trapping reaction. Although the fluctuations are larger for the smaller values of $T(0)$ and k' equal to 0.001 (Figure

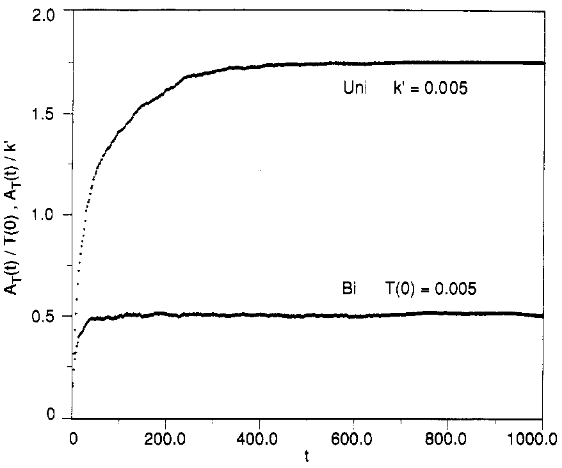

Figure 13. The same as in Figure 12, but with larger trapping rate and initial trap density.

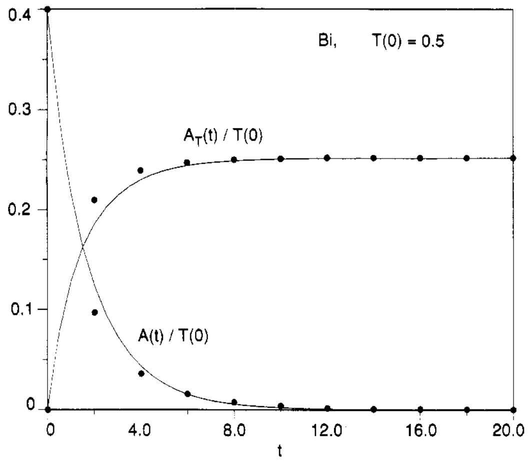

Figure 14. Simulation results (●) on both free A and trapped A (A_T) populations are plotted vs time and compared with ideal mixing MFT ($b = {}^4/_3$) for bimolecular trapping.

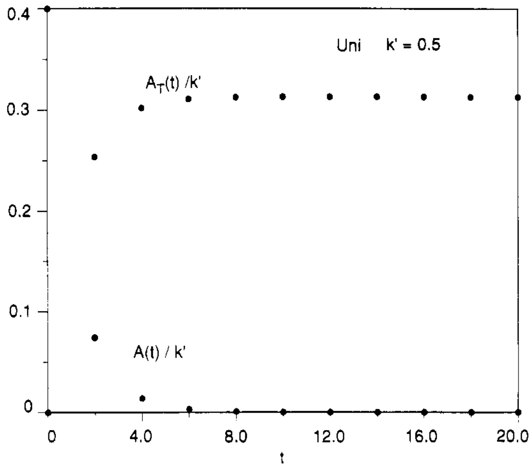

Figure 15. Simulation results (●) on both free A and trapped A populations are plotted vs time for unimolecular trapping.

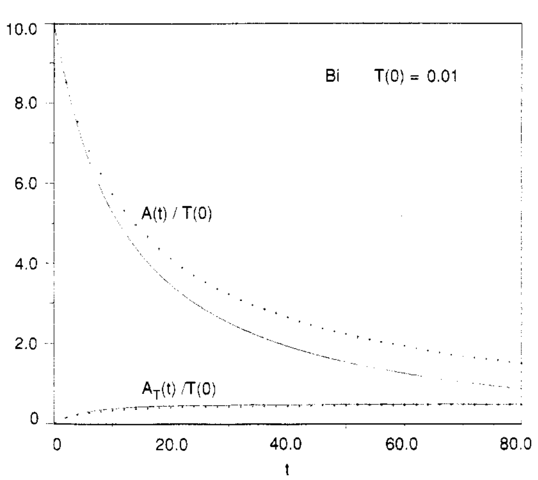

Figure 16. The same as in Figure 14, except that now the simulation results are indicated by (+), the initial trap density is much smaller, and the ratio $A(0)/T(0)$ is much larger. Note that population crossing has not occurred, even after 80 time steps. Also note the divergence of $A(t)/T(0)$ from the computed MFT curve.

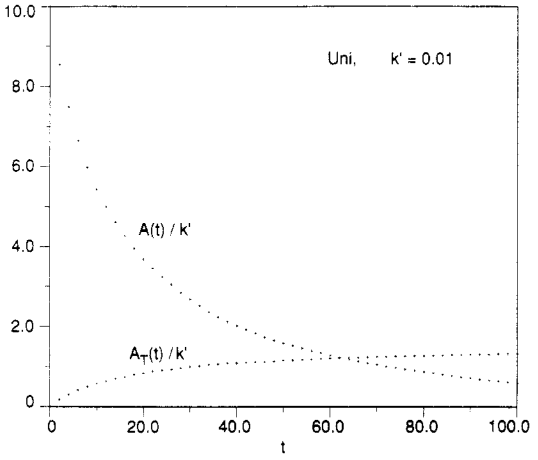

Figure 17. The same as in Figure 15, except that now the simulation results are indicated by (+), the trapping rate is much smaller, and the ratio $A(0)/k'$ is much larger. Note that in contrast to Figure 15 population crossing has occurred after 65 time steps.

13), it is quite remarkable how soon the mean of $A_T(t)/T(0)$ in a bimolecular trapping reaction lies close to its limiting value. In Figures 14–17 the free and trapped particle concentrations are depicted as a function of time for both types of trapping/annihilation reactions. The simulation results for bimolecular trapping/annihilation reactions are compared with mean field theory (full lines) in Figures 14 and 16 for different initial free particle and trap densities. With two exceptions the overall agreement is excellent. The first of these discrepancies appears at very short times, up to about eight time steps, and can be attributed to the treatment of time as a continuous variable in our mean field theory. The second disagreement (see Figure 16), which is real, occurs between the calculated and simulated free particle concentrations $A(t)$ at low trap densities ($T(0) = 0.01$). The simulations of $A(t)$ clearly show deviations from mean field behavior although the density of trapped particles $A_T(t)$ conforms accurately to this theory at all times!

In the Introduction it was noted that for the catalytic annihilation reaction

$$A + B \rightarrow B + C \tag{3.7}$$

in which the A's can freely diffuse and the B's are in a static random configuration, the long time asymptotic behavior of A is given by the Donsker–Varadhan form[20–25]

$$A(t) \sim \exp(-t^{d/(d+2)}) \tag{3.8}$$

where d is the spatial dimension. As demonstrated in Figures 18

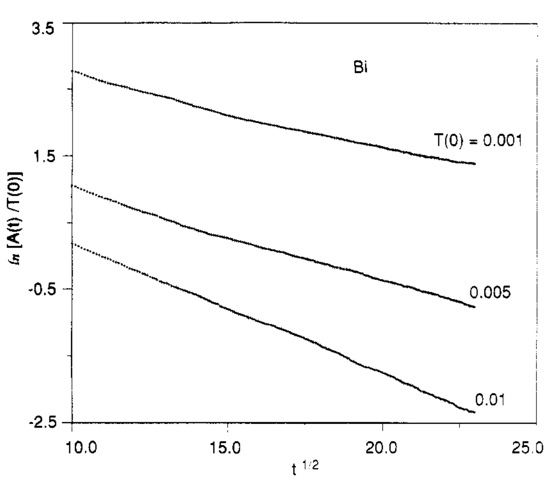

Figure 18. Simulation results for recombination plus bimolecular trapping, indicating that the stretched exponential decay $A(t) \sim \exp(-t^{\alpha})$ with $\alpha \sim {}^1/_2$ seems to describe the kinetics adequately.

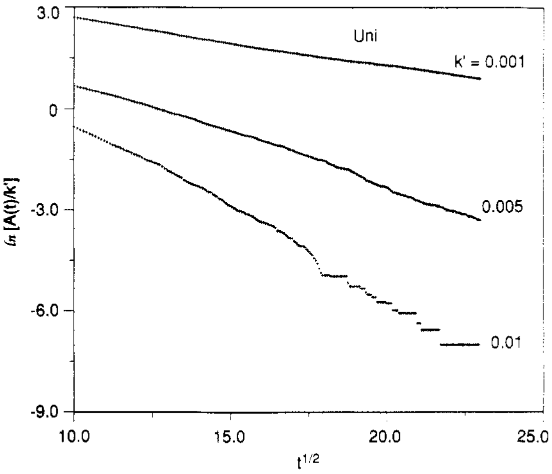

Figure 19. The same as in Figure 18, except that recombination plus unimolecular trapping has been simulated.

and 19, this stretched exponential decay gives a good account of both bimolecular and unimolecular trapping/annihilation ($d = 2$), even though neither reaction mechanism conforms exactly to eq 3.7. The physical explanation behind eq 3.8 is that at long times the A particles which have avoided annihilation by traps (B) are those which have wandered into large trap-free regions, regions which occur with an exponentially small probability. It is the balance between these two opposing factors—the long lifetime in a void vs the small probability of locating such a void—which produces the stretched exponential.

IV. Discussion

What is perhaps the most surprising result of our study is that the MFT perfect mixing analysis agrees precisely with the computer simulations of bimolecular trapping, at least as far as the trapped A population $A_T(t)$ is concerned. Furthermore, this exact conformity holds over a very large range of initial conditions ($A(0)$, $T(0)$). The explanation for this ideal behavior is as follows. At high trap densities, the reaction is essentially complete before spatial correlations have had a chance to develop, while at low trap densities the initially important spatial correlations are between free A's and density fluctuations tend to be "self-rectifying"; i.e., a local enhancement in $A(t)$ results in an increase in the free A recombination rate, while the converse is true for a local diminution in A. The key point is that at longer times the traps are flooded with an excess of A's with the consequence that exactly half of the initial T population has been converted into A_T (save for relatively small statistical fluctuations); this is because a free A has an equal probability of reacting with a T or an A_T. So far as A_T is concerned, the latter stage of the reaction consists entirely of the random reshuffling of equal numbers of A_T and T particles, there being no correlation between a trapping event and an A–A_T annihilation event. Not surprisingly this argument breaks down for recombination with unimolecular trapping, for in this case there are no vacant traps and the A_T population is evolving in such a manner as to be highly correlated with the local free A density. However, the interplay of the various spatial correlations is rather complex and deserves some comment. For high trapping rates the situation is identical with the bimolecular case with a large initial trap density, and MFT should again hold. For lower trapping rates and large $A(0)$, we are in the self-rectifying regime at short times and $A(t)$ will be more or less uniform. However, as A_T's begin to form there will evolve a correlation between A_T and A: an A_T enveloped in a region deficient in A will last longer than one surrounded by an excess of A. This effect is partially compensated by the fact that the odds of an A_T appearing in some region are raised by enhancing the number of A's in that region. This implies that even at long times the free A bimolecular recombination competes with A–A_T annihilation, and one anticipates a more gradual approach to the stationary state than is observed in bimolecular trapping. This feature, which appears in our simulations, might prove most useful to an observer attempting to distinguish between the two trapping mechanisms by simply monitoring $A(t)$ or $A_T(t)$.

As mentioned earlier, allowing for reversible trapping should have the same effect as our incorporation of a finite "staying" or "sticking" probability; i.e., a particle now has a finite chance of remaining fixed during the passage of a unit of time. Note, however, that this "stick" algorithm corresponds to unimolecular trapping only; for reversible bimolecular trapping we expect the kinetics to be similar, though not identical. In both instances one anticipates $A(t) \sim t^{-1}$ for sufficiently long times.

A most curious and puzzling observation is the rapid, rather than very gradual, appearance of stretched exponential ($\exp(t^{-\alpha})$, $\alpha = 1/2$) decay in $A(t)$ for both uni- and bimolecular trapping/annihilation. The Donsker–Varadhan mechanism requires the presence of large regions completely devoid of traps, and such regions are extremely rare in a random trap configuration. In the unimolecular case, however, traps are continually being formed by diffusing A's which have developed spatial correlations and so one anticipates correlated traps. Furthermore, the diffusing particles can excavate their own trap-free regions through the A–A_T annihilation mechanism. In the bimolecular case the traps are immortal, and so one might expect no acceleration of stretched exponential behavior in $A(t)$. Note, however, that those free A's which remain at long times are those particles which have tended to avoid one another so as not to annihilate, and this is in addition to having avoided an encounter with a T or A_T. One might expect this correlated A population to be more efficient at locating large trap-free voids than an equivalent number of uncorrelated particles.

At any rate, the most important findings of this study are as follows. Irreversible trapping has a profound effect on diffusion-limited bimolecular recombination processes, the details of the trapping mechanism are indeed discernible through the "observable" (single particle density) kinetics, and while certain features of the reaction can be computed very accurately from a simple mean field theory, other aspects are dominated by large, anomalous fluctuations.

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Appendix: Rate Constants for Annihilation Reactions with and without Traps

Consider a square lattice with a random distribution of A's at time t so that no more than one particle can occupy each site. Let the normalized density of free particles be $A(t)$ which is also the probability that a site is occupied. Pick any site S, which may be free or occupied. We ask what is the probability that the same site will be occupied, at the next time step after any annihilations have taken place? Assuming complete random mixing, this probability is also the normalized density $A(t+1)$ at the next time step after allowing for possible annihilation by pairs. The rate constant for free particle annihilation is then calculated from the difference between the densities $A(t+1)$ and $A(t)$ at successive time steps. We discuss this for free particle annihilations with zero staying probability before considering annihilations with a finite staying probability. The arguments can be readily, but tediously, extended to annihilation reactions with trapping; as expected intuitively, the presence of trapped A's does not alter the bimolecular rate constant for free annihilation which, however, does depend on the staying probability; see eq A.7.

Annihilation with Zero Staying Probability. The probability that the site S is occupied at time t is $A(t)$. When the staying probability p_s is zero, it is irrelevant whether the site S is actually free or not; if it is occupied the particle will move to one of four neighboring sites with probability $1/4$ in the next time step and make no contribution to the probability that the site S is occupied. At time t, the number of neighboring sites that are occupied can range from zero to four. If all of the neighboring sites are empty at time t, the central site S obviously cannot be occupied at time $t + 1$. There are four ways of realizing the occupation of only one neighboring site which occurs with probability $A(t)$. The probability that a site (neighboring or not) is unoccupied is $(1 - A(t))$. Hence, the contribution of a solitary neighbor to the probability that the central site S will be occupied at time $t + 1$ is $4(1/4)A(t)(1 - A(t))^3 = A(t)(1 - A(t))^3$. Two occupied neighboring sites will lead to single occupancy of the central site at the next time step only if one of these particles moves in; the probability that this occurs is easily calculated to be $2[4!/(2!\cdot 2!)](1/4)(3/4)A(t)^2(1 - A(t))^2 = (9/4)A(t)^2(1 - A(t))^2$. When three or four neighboring sites are occupied, pairwise annihilation ensures that only one or three of these particles moving into the central site will lead to single occupancy after annihilation at the next time step; the probabilities of this occurring are found to be $(7/4)A(t)^3(1 - A(t))$ and $(15/32)A(t)^4$, respectively. Adding all of these contributions we find

$$A(t+1) = A(t)(1 - A(t))^3 + (9/4)A(t)^2(1 - A(t))^2 + (7/4)A(t)^3(1 - A(t)) + (15/32)A(t)^4 \quad (A.1)$$

Subtracting $A(t)$ and going over to the limit of a continuous time variable, we have

$$[\mathrm{d}A(t)/\mathrm{d}t]_{NT} = -(3/4)A(t)^2 + (1/4)A(t)^3 - (1/32)A(t)^4 \quad (A.2)$$

where the subscript NT stands for no trapping. This is eq 2.4a of our paper which implies that the rate constant k for free particle annihilation to $O(A(t)^2)$, assuming random mixing, is $3/4$. It is simple to extend this to the case of bimolecular annihilation with traps, where it is found that

$$\mathrm{d}A(t)/\mathrm{d}t = [\mathrm{d}A(t)/\mathrm{d}t]_{NT} - T(0)[A(t) - (3/4)A(t)^2 + (1/4)A(t)^3 - (1/32)A(t)^4] \quad (A.3)$$

where $[\mathrm{d}A(t)/\mathrm{d}t]_{NT}$ is given by eq A.2. From the coefficients of the second-order terms we see that the binary rate constant k for free particle annihilation remains equal to $3/4$ even in the presence of trapped particles, while the rate constant k_T for annihilation of trapped particles with free particles is unity.

Annihilation with Traps When the Staying Probability Is Not Zero. Here it is necessary to consider whether the site S is occupied or not. For free particle annihilation instead of (A.1) we have

$$A(t+1) = (c_1 + c_1')A(t)(1 - A(t))^4 + (c_2 + c_2')A(t)^2(1 - A(t))^3 + (c_3 + c_3')A(t)^3(1 - A(t))^2 + (c_4 + c_4')A(t)^4(1 - A(t)) + c_5A(t)^5 \quad (A.4)$$

where c_i and c_i' are the coefficients of the contributions from i sites, including the central site S, at time t to the probability that the site S is occupied by a free particle at time $t + 1$; the prime distinguishes the moves in which the central site S is unoccupied, at time t, from the moves in which it is filled. It is found that

$$c_1' = (1 - p_s)$$

$$c_1 = p_s$$

$$c_2' = (3/4)(3 - 2p_s - p_s^2)$$

$$c_2 = (1 + p_s + 2p_s^2)$$

$$c_3' = (1/4)(7 - 3p_s - 3p_s^2 - p_s^3)$$

$$c_3 = (3/4)(3 + 3p_s^2 + 2p_s^3)$$

$$c_4' = (1/32)(15 - 4p_s - 6p_s^2 - p_s^4 - 4p_s^3)$$

$$c_4 = (1/4)(7 - p_s + 3p_s^2 + 5p_s^3 + 2p_s^4)$$

$$c_5' = (1/256)\{p_s[(3 + p_s)^4 + 6(3 + p_s)^2(1 - ps)^2 + (1 - p_s)^4] + 4(1 - ps)^2[(1 - p_s)^2(3 + p_s) + (3 + p_s)^3]\}$$

$$c_5 = 0 \tag{A.5}$$

Subtracting $A(t)$ from eq A.4 and going over to the limit of continuous time, it is found that

$$[\mathrm{d}A(t)/\mathrm{d}t]_{\mathrm{NT}} = (-4 + \alpha_2)A(t)^2 + (6 - 3\alpha_2 + \alpha_3)A(t)^3 + (-4 + 3\alpha_2 - 2\alpha_3 + \alpha_4)A(t)^4 + (1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5)A(t)^5 \tag{A.6}$$

where $\alpha_i = c_i + c_i'$ and, in particular, the rate constant for free particle annihilation

$$k = (4 - \alpha_2) = 3/4 + p_s/2 - (5/4)p_s^2 \tag{A.7}$$

Extending this argument to bimolecular annihilation with traps, we find that

$$\mathrm{d}A(t)/\mathrm{d}t = [\mathrm{d}A(t)/\mathrm{d}t]_{\mathrm{NT}} - T(0)[c_1'A(t) + (-3c_1' + c_2')A(t)^2 + (3c_1' - 2c_2' + c_3')A(t)^3 + (-c_1' + c_2' - c_3' + c_4')A(t)^4] \tag{A.8}$$

where $[\mathrm{d}A(t)/\mathrm{d}t]_{\mathrm{NT}}$ is now given by (A.6). It follows that the rate constant for free particle annihilation remains unchanged in the presence of traps while the rate constant for the annihilation of trapped particles is given by

$$k_T = c_1' = 1 - p_s \tag{A.9}$$

It is readily verified that when $p_s = 0$, eq A.8 reduces to eq A.3. Another check on these calculations is provided by the limiting condition of $p_s = 1$, when all of the coefficients of the various powers of $A(t)$ in (A.6) and (A.8) must be zero. This also implies that in this limit k and k_T are zero.

Since $A(t) \leq 1$, the long time behavior of $[\mathrm{d}(1/A(t))/\mathrm{d}t] = -(1/A(t))^2$, $[\mathrm{d}A(t)/\mathrm{d}t]$ is governed by the leading term, $(4 - \alpha_2)$, which has a maximum at $p_s = {}^1/_5$. This is the staying probability at which a crossover in the curves $1/A(t)$ vs t is predicted to occur for free particle annihilation in the absence of traps.

Influence of Polar Solvents on Reaction Dynamics. Photoisomerization Studies of Dihydroxystilbene

N. S. Park and D. H. Waldeck*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260 *(Received: April 17, 1989; In Final Form: July 19, 1989)*

The photoisomerization kinetics of 4,4′-dihydroxystilbene in polar solvents, *n*-alkyl alcohols and *n*-alkanenitriles, was investigated as a function of temperature at ambient pressure. Although it is possible to define an activation barrier within a restricted set of solvents, the activation energy depends on both the magnitude and the dynamics of solvation. Comparison of these results with earlier work on *trans*-stilbene and 4,4′-dimethoxystilbene demonstrates their generality and probes effects of hydrogen bonding with the hydroxyl group. A comprehensive view of the reaction dynamics where the solvent polarization field is intimately coupled to the "intramolecular" reaction coordinate is discussed.

Introduction

Polar solvents can have a dramatic influence on chemical reaction rates and chemical reaction mechanisms. Recent studies of electron-transfer reactions, both intermolecular and intramolecular, demonstrate the importance of both the magnitude of solvation and the time dependence of solvation on reaction rates.[1-5] The relative time scales of solvation and reaction determine the friction experienced for the electron transfer. The dynamics of solvation also plays an important role in reactions involving motion of nuclei, in particular isomerization reactions.[6-9] The present work extends these earlier studies, on stilbene and 4,4′-dimethoxystilbene, to the investigation of the photoisomerization of 4,4′-dihydroxystilbene in both *n*-alkyl alcohols and *n*-alkanenitriles.

The photoisomerization of stilbene and its analogues[7-16] provides

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