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LETTERS

Modeling of Diffusion-Reaction Processes Involving Geminate Radical Pairs

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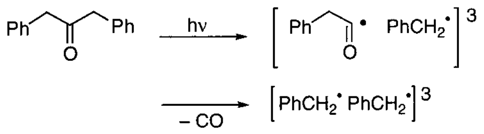
A Markovian theory is developed to study the efficiency of diffusion-reaction processes involving geminate radical pairs moving on the surface of a catalyst (e.g., zeolite) support. Results obtained for the simplest (lattice) system are corroborated by Monte Carlo calculations, and these are extended to study the effect of system size. A kinetic model is developed to account for the results obtained and leads to the general conclusion that the photochemical generation of a triplet pair, followed by the subsequent diffusion and eventual recombination of the radicals R↑ and R↓, lengthens the mean reaction time by a factor of ∼2, relative to the case in which R↑ and R↓ are assumed to be present at the very outset.

In most photochemical reactions, geminate radical pairs are produced as triplet pairs. Such triplet pairs, in which both radicals have the same spin, are inert to radical−radical recombination reactions. A "spin flip" to a reactive singlet pair must occur before the radicals can combine. Although several mechanisms exist for intersystem crossing, such a spin flip can occur through some magnetic effect in the environment acting on one or both of the spins.[1]

Recent experimental studies on the photochemical production of geminate radical pairs and their subsequent fate when diffusing on/in the surface/interior of a zeolite have documented the ability to control reactions in the presence or absence of magnetic fields or magnetic impurities.[2−6] In this report, we mobilize a recently introduced approach,[7−8] based on the theory of finite Markov processes, to calculate numerically exact values of the mean walklength $\langle n \rangle$ of two simultaneously diffusing triplet pairs before a "spin flip" occurs and permits a singlet pair to react, eventually, upon first encounter. We also present the results of complementary Monte Carlo calculations and develop an analytic approach for the mean-field case to compare the numerical results with the predictions of classical kinetic theory.

Consider, for definiteness, the photochemical reaction involving 1,3-diphenyl acetone



For the case in which this reaction takes place on the surface of a zeolite at some point of which there is a site S at which a spin flip can occur (e.g., a zeolite site with a heavy-metal cation such as Tl), the sequence of events diagrammed in Figure 1

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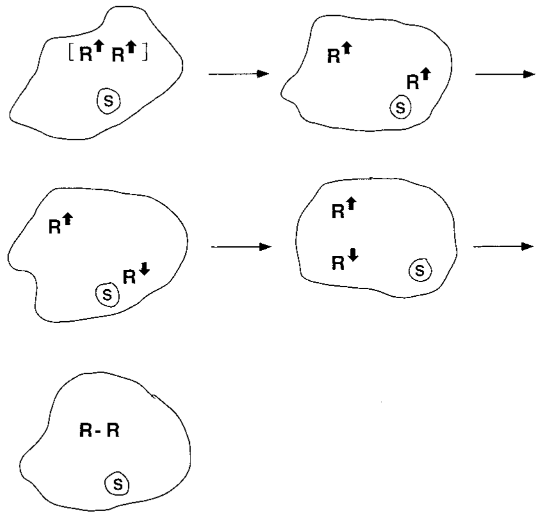

Figure 1. A schematic representation of a geminate radical pair recombination reaction.

can be envisioned. Corresponding to this sequence, the following model is defined:

$$\mathrm{X1} + \mathrm{S} \rightarrow \mathrm{X2} \tag{1}$$

where X1 = R↑ and X2 = R↓, and

$$\mathrm{X1} + \mathrm{X2} \rightarrow \text{product } (\mathrm{R{-}R}) \tag{2}$$

We also allow for the following processes:

$$\mathrm{X2} + \mathrm{S} \rightarrow \mathrm{X1} \tag{3}$$

and

$$\mathrm{X1} + \mathrm{X1} \rightarrow \mathrm{X1} + \mathrm{X1} \tag{4}$$

$$\mathrm{X2} + \mathrm{X2} \rightarrow \mathrm{X2} + \mathrm{X2} \tag{5}$$

In steps 4 and 5, the collision of like radicals simply resets the two radicals to their previous positions. Equation 2 makes the implicit assumption that $\mathrm{S}{-}\mathrm{T}_0$ intersystem crossing is fast on the hopping time scale.

In the approach developed here, all possible reactant pairs are considered. That is, at any given time, there may be present two X1 species, two X2 species, or the pair X1 and X2. Whatever the case, the two species ([X1, X1], [X2, X2], or [X1, X2]) are regarded to be diffusing simultaneously on a surface with the outcome of collisions between two species or the encounter of a given species with the "trigger site" S, specified by eqs 1−5. The surface itself is represented by a lattice of periodically repeating units; specifically, we consider an $n \times n$ square planar lattice subject to periodic boundary conditions. The site S at which the spin flip occurs is stationary and comprises one of the sites of the lattice.

The basis of the Markovian approach reported in ref 1 is classification of all initial configurations of particles on the lattice and all concerted motions corresponding to each such configuration into symmetry-distinct states. The probability of realizing each new configuration is then assigned from which one can construct the transition probability matrix **Q** and, thence, determine the fundamental matrix $\mathbf{N} = (\mathbf{I} - \mathbf{Q})^{-1}$ of the theory of finite Markov processes, where **I** is the identity matrix. The mean walklength $\langle n \rangle$ (as well as higher-order moments of the underlying probability distribution function) can then be extracted from **N**, and the temporal behavior of the system determined from the eigenvalues of **N**. We impose the condition that when recombination of the geminate radical pairs occurs (step 2), the process terminates.

TABLE 1: A Comparison of the Values of $\langle n \rangle$ as Obtained from the Markovian and Monte Carlo Approaches (calcd) or Estimated from the Mean Field Model, Eq 13 (est)

lattice	k^{-1}	k'^{-1}	$\langle n \rangle$ (calcd)	$\langle n \rangle$ (est)	percent
3 × 3	9	8	18.81	18.56	1.35
4 × 4	18.31	22.22	50.53	49.49	2.06
5 × 5	31.67	26.07	63.68	61.24	3.83
6 × 6	49.24	52.67	124.63	119.07	4.46
7 × 7	71.62	56.65	142.50	133.97	5.99
8 × 8	98.59	98.38	238.10	224.45	5.73
9 × 9	130.60	99.78	257.19	237.42	7.69
10 × 10	167.41	159.70	394.80	366.65	7.13

To illustrate the cases considered here, consider first the results obtained on the simplest lattice, a 3 × 3 square-planar lattice, with a single "trigger site" S and subject to periodic boundary conditions. For the reaction sequence 1−5, the mean walklength before termination of the reaction (i.e., the recombination step 2) is then found to be $\langle n \rangle = 18.814$. This value can be compared with the value of $\langle n \rangle$ calculated for the case of two simultaneously diffusing radicals,[7] R↑ and R↓, where an intervening step involving a "spin flip" is not needed to create a singlet pair: $\langle n \rangle = 8$. Similarly, it can be compared with the value of the $\langle n \rangle$ calculated when one reactant of the pair, R↑ and R↓, is assumed to be stationary:[7] $\langle n \rangle = 9$. We are immediately led to the conclusion that the photochemical generation of a triplet pair, followed by diffusion of the two radicals until one undergoes a spin flip at the site S, followed by subsequent diffusion and eventual recombination of the radicals R↑ and R↓, lengthens the mean walklength $\langle n \rangle$ (and hence the mean reaction time τ) by a factor of ∼2, relative to the case in which R↑ and R↓ are assumed to present from the very outset. Because the Markovian theory, which was mobilized to calculate the $\langle n \rangle$, leads to numerically exact values of $\langle n \rangle$, one has confidence in the prediction of the doubling time noted above, given the assumptions of the model and the lattice considered.

The problem described above can also be studied via direct Monte Carlo simulations. A large number of realizations ($\sim 2 \times 10^6$) was carried out, covering all possible distinguishable initial configurations. The result of the Monte Carlo study for the 3 × 3 lattice, $\langle n \rangle = 18.81$, is fully in accord with the value obtained in the Markovian analysis.

To examine the effect of system size, the Monte Carlo simulations were extended to larger $n \times n$ square planar lattices, with $4 \leq n \leq 10$; the results are reported in Table 1 (fourth column). Two conclusions may be drawn from these more extensive calculations. First, there is further support for the conclusion reached in the above discussion, namely, that there is an approximate doubling of the reaction time when geminate species R↑ and R↑ are created initially versus the case where R↑ and R↓ are present at time $t = 0$ (either for the case where one radical is stationary or both are free to diffuse, for which reaction times were taken from ref 7). And second, the increase in $\langle n \rangle$ is smaller than the increase in the total number, $L = n \times n$, of lattice sites available to the diffusing reactants, an effect illustrated in Figure 2 (full lines).

It is interesting and relevant to compare the above results with the predictions of a classical, mean-field kinetic approach,

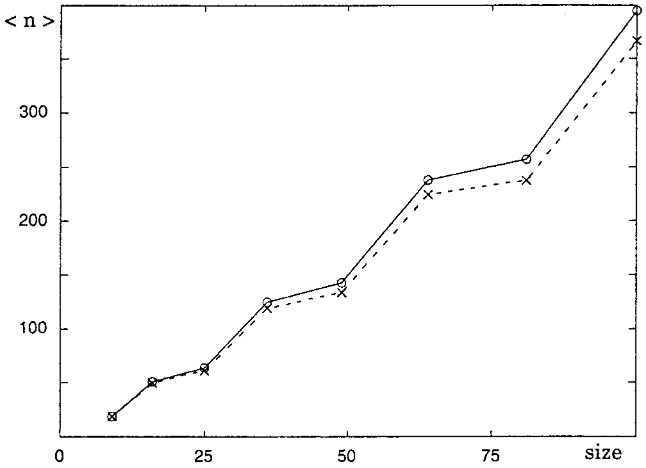

Figure 2. Dependence of reaction time $\langle n \rangle$ on the lattice size. Full and dotted lines refer, respectively, to the Markovian/Monte Carlo results and to the estimates based on the mean field model.

wherein concentration fluctuations are suppressed. Define the doublet configurations as

$$\mathrm{a} = [\mathrm{X1}, \mathrm{X1}]$$
$$\mathrm{b} = [\mathrm{X1}, \mathrm{X2}]$$
$$\mathrm{c} = [\mathrm{X2}, \mathrm{X2}]$$

Then, the kinetic scheme, eqs 1−5, above can be represented by

$$\mathrm{a} \underset{k}{\overset{2k}{\rightleftharpoons}} \mathrm{b} \tag{6}$$

$$\mathrm{c} \underset{k}{\overset{2k}{\rightleftharpoons}} \mathrm{b} \tag{7}$$

$$\mathrm{b} \xrightarrow{k'} \text{product} \tag{8}$$

with $k = {}^1/_9$ and $k' = {}^1/_8$ for the 3×3 lattice. The evolution equations are

$$\dot{a} = -2k[\mathrm{a}] + k[\mathrm{b}] \tag{9}$$

$$\dot{b} = -2k[\mathrm{a}] + 2k[\mathrm{c}] - 2k[\mathrm{b}] - k'[\mathrm{b}] \tag{10}$$

$$\dot{c} = -2k[\mathrm{c}] + k[\mathrm{b}] \tag{11}$$

The coefficient matrix **M** corresponding to eqs 9−11 is

$$\mathbf{M} = \begin{bmatrix} -2k & k & 0 \\ 2k & -(2k + k') & 2k \\ 0 & k & -2k \end{bmatrix} \tag{12}$$

and the corresponding eigenmatrix is

$$\begin{bmatrix} -2k - W & k & 0 \\ 2k & -(2k + k') - W & 2k \\ 0 & k & -2k - W \end{bmatrix} = 0$$

This leads to the eigenvalue equation

$$W^2 + (4k + k')W + 2kk' = 0 \tag{13}$$

from which the mean time for the 3×3 lattice is determined to be

$$\tau = W^{-1} = 18.560$$

Given a unit displacement (“hopping”) time, this estimate is in surprising agreement with the exact value noted above, namely, $\langle n \rangle = 18.814$. The agreement extends to larger lattices as well, as shown in Table 1 (fourth column) and in Figure 2 (dotted lines). The rate constants, k and k', for these lattices are estimated by identifying the corresponding reaction times, k^{-1} and k'^{-1} to the mean walklength $\langle n \rangle$ taken from ref 7. The values so obtained are given in the second two columns of Table 1.

Although there exist at present no explicit experimental data on the magnetically induced spin exchange and reaction of radicals diffusing on zeolite lattices, there is an earlier study of paramagnetic interactions of triplet radical pairs with nitroxide radicals in which an unusual “antiscavenging” effect was observed.[9] This study, carried out in solution, involved radicals and scavenger undergoing random (simultaneous) diffusion prior to chemical scavenging of geminate radicals and nitroxide. The analytical methods introduced in ref 7 and exploited here were generalized in ref 8 to deal with diffusion-reaction processes involving three simultaneously diffusing reactants. It is this generalization that will be implemented in future work to examine the experimental problem studied in ref 9.

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