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EFFECTS OF SPATIAL CONFINEMENT ON THE REACTIVITY IN ORGANIZED LIQUID MEDIA

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Abstract - The influence of spatial confinement of reactants in organized liquid media leads to kinetic rate laws which differ from those discussed in homogeneous solution. We consider in this paper how reactivity correlates with different microstructures such as micellar aggregates and colloidal semiconductors. Strategies are outlined to design systems which achieve high reaction rates and product yields as well as selectivity. The kinetics models are tested by Monte Carlo simulations and compared to experimental results.

INTRODUCTION

Recently, there has been a surge of interest in the reactivity in organized liquid media.[1] A wide variety of organized assemblies such as cyclodextrins, micelles, microemulsions and vesicles are presently employed as hosts in numerous chemical reactions. An important goal of these studies is to correlate reactivity with these different types of microstructures. In many cases the role of the host aggregate is simply to solubilize the reactant species which are insoluble in the bulk solvent. More recently, the quest for high reaction rates and efficiency has led to the application of molecular engineering to optimise the performance of these systems. For example, functional surfactants display cooperative effects and rate enhancements approaching enzyme catalysis have been achieved with such assemblies. Another new research front is that of colloidal semiconductors.[2] Here, the very rapid nature of charge carrier motion within the assembly and the large ratio of surface to bulk atoms can be exploited to improve the yield of heterogeneous redox reactions.

In this paper we examine the effect of spatial confinement of the reactants on the kinetics of bimolecular processes in organized assemblies. It is shown that for fast reactions the conventional rate laws established for homogeneous solutions cannot be applied. Monte Carlo simulations are presented which allow to unravel the nature of diffusion controlled processes in confined reaction space. The results which emerge from these considerations are useful to model experimental results and should provide incentives to elaborate strategies for designing systems with improved reaction efficiency and selectivity.

DIFFUSION MEDIATED REACTIONS IN COMPARTIMENTALIZED SYSTEMS

We consider the irreversible bimolecular process

$$A + B \xrightarrow{k} \text{products} \tag{1}$$

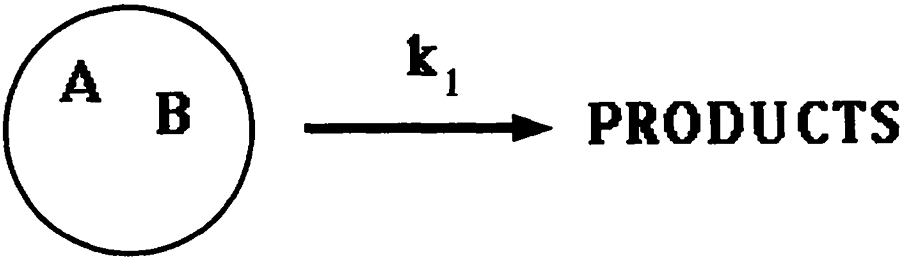
and address the question how the sequestering of the reactants in a host aggregrate will affect the reaction kinetics. In homogeneous solution the differential rate law is:

$$-\frac{dc_A}{dt} = k_2\, c_A \cdot c_B \tag{2}$$

The reaction order is 2 and k_2 has the units $M^{-1}s^{-1}$, or alternatively cm^3S^{-1} if concentrations are expressed in units of molecules/cm^3. We shall now explore the kinetic consequences of confining the reactants within an ensemble of small spheres such as a micelle or a microemulsion droplet.

We first consider the case where the reaction volume, a sphere of radius R, contains only two reactive molecules: A and B, Figure 1. The reactants are assumed to be hard spheres of radii r_A and r_B moving with the diffusion constants D_A and D_B respectively. They are initially randomly distributed throughout the volume of the sphere. We shall restrict our considerations in the following to cases where the reaction is diffusion controlled and hence occurs upon the first encounter of A and B. The model is, however, extendable to slower reactions by introducing a probability factor corresponding to the reciprocal of the average number of collisions which are required to occur between A and B before the chemical transformation takes place. Furthermore, when discussing the effects of confinement on chemical kinetics it is implied that the reaction time is much shorter than the time required for exchanging the reactants between different host aggregates. In situations where the opposite is true, i.e. the exchange is much faster than the reaction, there are no compartimentalization effects to be expected and the kinetics follow the same rate law as in homogeneous solution.

FIGURE 1



The goal of our present analysis is to derive the time law for the disappearance of A - B pairs, sequestered in very small spherical reaction volumes, due to the bimolecular reaction (1). The quantitiy of interest is E (t), the probability that the A - B pair has not reacted at time t. Unfortunately, it is impossible to derive an analytical expression which would allow for the calculation of this survival possibility. The problem can, however, be solved analytically[3] if it is assumed that one of the reactants, say A, is immobilized in the center of the sphere while the other undergoes random motion. One obtains in such a case:

$$E(t) = \sum_{n=1}^{n=\infty} C_n \exp\left(-X_n^2 D_B t/r_o^2\right) \tag{3}$$

where $r_o = R - r_B$ and the values of X_n are roots of the equation:

$$X_n \operatorname{cotg}\left((1 - d/r_o)X_n\right) = 1 \tag{4}$$

The coefficients of this series are given by the expression:

$$C_n = \frac{6}{\left(\frac{d^2}{r_o^2} - \frac{r_o}{d}\right) X_n^2 \left(1 - \frac{r_o}{d} \frac{X_n^2}{1 + X_n^2}\right)} \tag{5}$$

where $d = r_A + r_B$.

Equation (3) has been discussed in connection with intramicellar electron- and energy transfer reactions.[3] If the radius of the micelle is significantly larger than that of the reactants, C_n approaches the value 1 and E(t) follows a simple exponential time law given by the first member of the series expansion in equation (3), i.e.

$$E(t) \simeq \exp\left(- X^2 D_B t/r_o^2\right) \tag{6}$$

In other words, the intramicellar reaction between single A ···B pairs is predicted to follow to a good approximation a first order process, the concentration of reactants decreasing in an exponential fashion with time:

$$\frac{C_A}{C_A^o} = E(t) = \exp(-k_1 t) \tag{7}$$

Since k_1 is a first order rate constant, it is expressed in units of s^{-1}. The value of k_1 represents the reciprocal average time for the reaction between a single pair of molecular solubilized in the micelle.

We conclude that the rate law for a bimolecular reaction involving single pairs in host aggregates is different from that observed for the same process in homogeneous solution. The effect of sequestering the reactants is to reduce the reaction order from 2 to 1. This is a consequence of the fact that in the compartimentalized systems the reaction volume is confined by the host aggregate whose interface with the bulk solvent represents a reflective boundary for the reactive species, limiting their diffusion and maintaining them in close proximity.

How can these proximity effects be exploited in order to optimize reaction rates? In order to answer this question one has to know how the size of the host aggregate affects the rate constant. Consider again the case of a reaction between two reactants A and B sequestered in a sphere of radius R as outlined in Figure (1). Our goal is to derive a relation between the size of the microsphere and the rate constant k_1 of the reaction.

We first employ the analytical solution given by Equation (3) where we have assumed that the reactant A is immobilized in the center of the sphere. Assuming furthermore that the size of the host aggregate is significantly larger than that of the reactants, Equation (7) can be applied which gives for the first order rate constant the expression:

$$k_1 = X_1^2 D/r_o^2 \tag{8}$$

The next step is to find the value of X_1 which is the first root of the transcendental equation (4). We can rewrite this equation as:

$$tg((1 - y)\,X_1) = X_1 \tag{9}$$

where $y = d/r_o$. Developing (9) in a Taylor series and keeping the first and second terms gives:

$$X_1^2 = 3y(1 - y)^3 \tag{10}$$

and therefore

$$k_1 = \frac{3dD}{(r_o - d)^3} \tag{11}$$

where D is the sum of the diffusion coefficient of A and B. Equation (11) shows that k_1 increases as the radius of the sphere decreases. In other words, the smaller the size of the host aggregate the larger will be the value of the rate constant. It may be argued that a size independent rate constant would be obtained if the value of k_1 is multiplied by the volume of the sphere. That this is not the case is evident from equation (11). Multiplying this expression by the volume $\frac{4}{3}\Pi r_o^3$ gives:

$$k_2 = \frac{4\Pi dD \cdot r_o^3}{(r_o - d)^3} \tag{12}$$

where k_2 has the units $cm^3 s^{-1}$, and formally corresponds to a second order rate constant. Clearly, k_2 is also a function of the radius of the host aggregate. Only for very large reaction volumes does the size dependency of k_2 vanish. This is illustrated by considering the limiting value of k_2 for $r_o \rightarrow \infty$:

$$\lim_{r_o \rightarrow \infty} k_2 = \lim_{r_o \rightarrow \infty} 4\Pi dD \frac{1}{(1 - d/r_o)^3} = 4\Pi dD \tag{13}$$

which yields the well known Smoluchowsky expression for diffusion controlled second order reactions in homogeneous media.

Several important conclusions can already be drawn from this approximate model. Care needs to be applied when comparing the kinetics of homogeneous second order reactions to processes involving pairs of reactants sequestered in host aggregates such as spherical micelles. In the latter case, the process follows a first order rate law. (Significant deviations from first order kinetics are expected only for conditions where the size of the micelle is commensurate with that of the reactants.) Description of intramicellar processes in terms of second order kinetics is inadequate in situations where the exchange of reactants between different micelles is slow compared to the reaction. In such a case the first order rate constant k_1 should be used for the kinetic description of the process. If k_1 is multiplied with the micellar volume one obtains the parameter k_2 which formally corresponds to a second order rate constant. In order to assess specific effects of the micellar microenvironment on the kinetics of a particular reaction, one might be tempted to compare k_2 with the rate constant for the same bimolecular process in homogeneous solution. If such a comparison is made the effect of micellar size on k_2 needs to be taken into account.

The model we have employed until now was based on the assumption that one of the reactants is immobilized in the center of the spherical reaction space. It is desirable to analyse the more realistic conditions where both reactants move freely within the host aggregate. Since there is no direct analytical solution to this problem we have performed numerical calculations using a Monte Carlo program. The movement of the two reactants is simulated by a random walk with a fixed step length Δl the average time required for each successive step is Δt and the diffusion coefficient is given by the relation:

$$D = \frac{\Delta l^2}{6\Delta t} \tag{14}$$

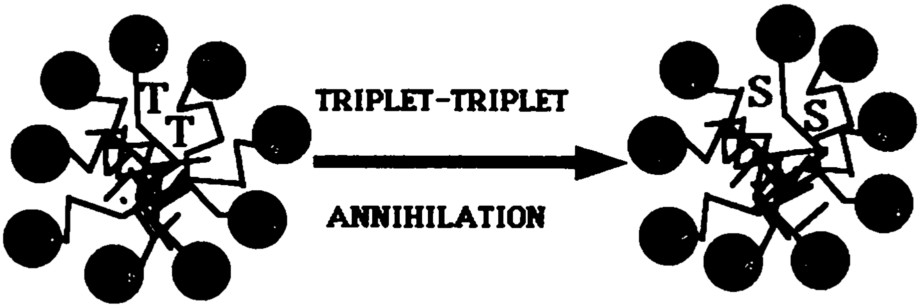
For simplicity we assume that the two reactants A and B have the same size and diffusion coefficient. The results of these calculations show that the survival probability of the A..B pairs decreases in an exponential fashion with time except in the very beginning of the reaction where the ln E(t) plot is nonlinear.[4] The extent of nonlinearity depends on the reaction parameters, i.e. the diffusion coefficient and the ratio d/r_o. Qualitatively, these results agree with the analytical solution of the approximate model discussed above. However, there are significant quantitative discrepancies between the two models, in particular with regard to the effect of the size of the reaction volume on the rate constant k_1. We shall now discuss the concrete case of intramicellar triplet annihilation in order to exemplify these differences.

Fast Intramicellar Reactions, Experimental Results and Monte Carlo Simulations

A large number of intramicellar reactions, including luminescence quenching, energy-and electron transfer as well as radical recombination processes occur on a time scale which is fast compared to intermicellar exchange of solubilisate molecules. These systems are therefore adequate to study the effects of compartimentalisation on the reaction kinetics. Overwhelming experimental evidence has confirmed that intramicellar processes involving a pair of reactants do indeed follow a first order rate law.[6] However, so far there has been no attempt to assess the influence of the micellar radius on the reaction rate constant k_1. We shall now consider the example of an intramicellar triplet annihilation reaction in order to analyse these size effects and to compare the prediction of the two models presented in the preceding section.

A schematic illustration of such a process is shown in Figure 2.

FIGURE 2
Intramicellar triplet annihilation
involving a pair of reactants



A case which has been studied experimentally in great detail is that of 1-bromonaphthalene in cetyltrimethylamonium bromide micelles (CTAB)[5]. The rate constant for the intramicellar triplet-triplet annihilation reaction is $k_1 = 2.8 \times 10^7 s^{-1}$. Inserting this k_1 value in equation (11) together with the micellar radius of 22Å and an interaction distance of $d = 7.4$Å, determined from a geometric model of the bromonaphthalene molecule, one derives a diffusion coefficient for bromonaphthalene of $D = 1.5 \times 10^{-7} cm^2 s^{-1}$. Inserting this value in the Stokes-Einstein equation

$$\eta = \frac{kT}{3\Pi dD} \qquad (15)$$

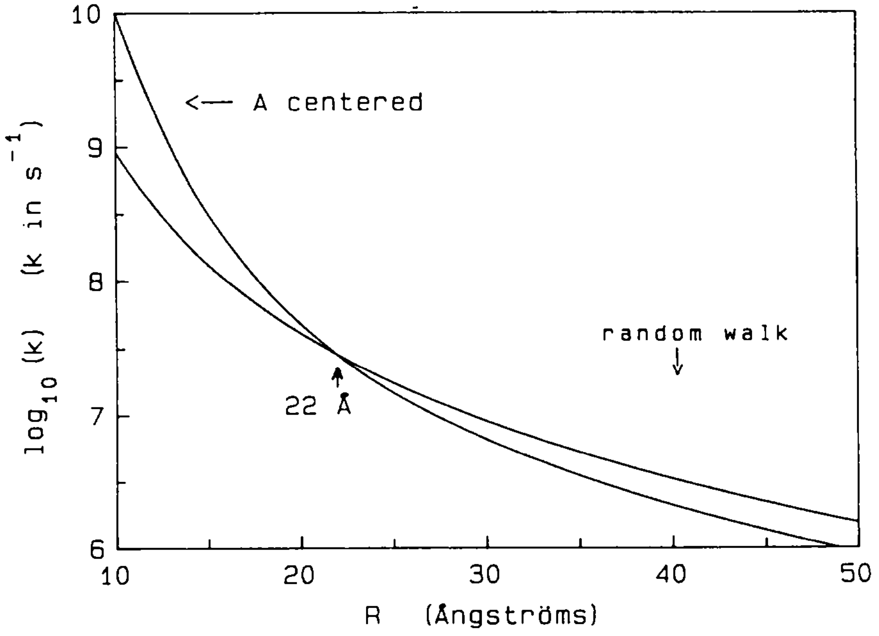
gives for the microviscosity present in the interior of CTAB micelles a value of 40 cp. This is higher than the η values determined from fluorescence depolarisation measurements which for CTAB range between 15 and 30 cp.

For comparison, the triplet-triplet annihilation process was simulated by Monte-Carlo calculations. Each random walk consisted of ca.10^5 steps and was repeated 2500 times. Details will be given elsewhere[4]. A diffusion coefficient of $D = 4.7 \times 10^{-7} cm^2 s^{-1}$ gave optimal agreement with the experimentally determined rate constant of $2.8 \times 10^7 s^{-1}$. This corresponds to a microviscosity of 13.6 cp in good agreement with the experimental results.

Using the diffusion coefficient $4.7 \times 10^{-7} cm^2 s^{-1}$ and the interaction diameter of 7.4Å we have performed Monte Carlo calculations to determine the effect of micellar radius on the rate constant k_1. The results plotted in a semilogarithmic fashion in Figure 3 show that the rate constant increases sharply with decreasing size of the micelle reaching a value of $10^9 s^{-1}$ when the radius of the aggregate is 10Å. The effects predicted by the approximate model are even more pronounced, particularly at small micellar radii where the reaction halftimes are in the picosecond domain. Figure 3 is illustrative in that it clearly demonstrates the consequence of immobilizing one of the reactants within the reaction space.

FIGURE 3

Effect of micellar radius on the rate of a diffusion controlled intramicellar reaction, the results obtained from Monte Carolo simulations are juxtaposed to the approximate analytical solution, eq. 11 where A is assumed to be located in the center of the sphere.



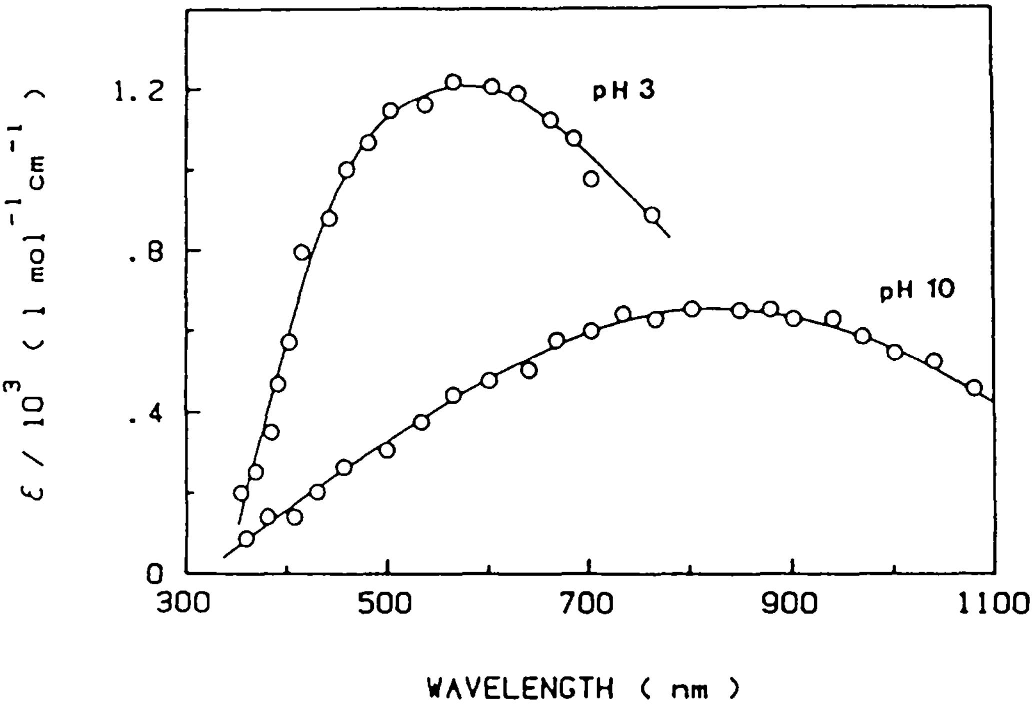
Charge Carrier Trapping and Recombination in Colloidal Semiconductor Particles

So far we have restricted our considerations to the case where only one reactant pair was present in the host aggregate. We shall now analyse a situation where the number of pairs exceed one. An illustrative example is that of electron-hole recombination in colloidal semiconductors.

These studies were carried out with colloidal titanium dioxide (anatase) particles having a diameter of 120 Å. Irradiation of such colloidal solutions in the presence of a hole scavenger such as polyvinyl alcohol or formate ions results in the accumulation of electrons in the particles. As a result, the solution assumes a beautiful blue color under illumination. It was found that up to 300 electrons can be stored in one TiO_2 particle. (A TiO_2 particle of 120 Å size has about 3600 conduction band states. Therefore, at most 10% of the available states are occupied by electrons.) The absorption spectrum of these stored electrons is shown in Figure 4:

FIGURE 4

Absorption spectrum of conduction band electrons in colloidal TiO_2 particles at pH 3 and pH 10.

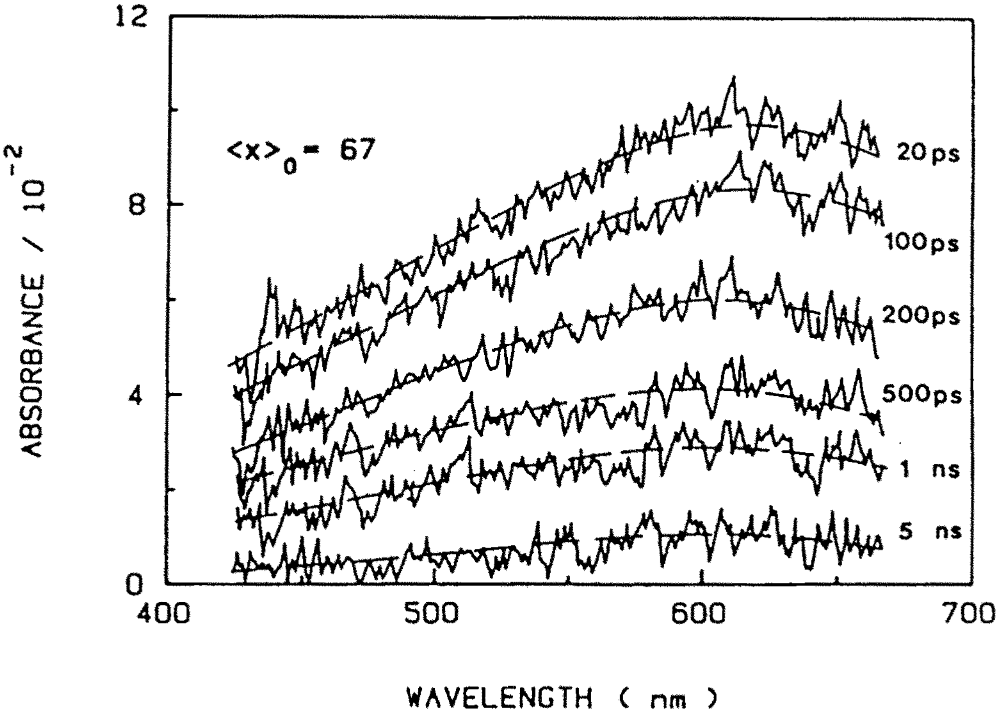


The electron spectrum was found to be sensitive to the pH of the solution. Under alkiline conditions the electron absorption is very broad and has a maximum around 800 nm. Lowering the pH to 3 produced a pronounced blue shift in the spectrum which under these conditions shows a peak at 620 nm. The sensitivity of the electron absorption to the solution pH would indicate that they are located in the surface region of the particles. This has been confirmed by recent ESR experiments which show that under acidic conditions the electrons are trapped at the TiO_2 surface in the form of Ti^{3+} ions[7]. Using redox titration, we have recently been able to determine the extinction coefficient of the trapped electrons[8]. For the colloidal solutions of pH 3 the extinction coefficient at 600 nm is 1200 $M^{-1}cm^{-1}$.

Taking advantage of the characteristic optical absorption of trapped electrons in the colloidal TiO_2 particles, we have recorded their recombination with free and trapped holes in the picosecond to microsecond domain[9]. Figure 5 shows the temporal evolution of the transient spectrum after excitation of TiO_2 with a frequency tripled (353 nm) Nd laser pulse of ca. 40 ps duration.

FIGURE 5

Transient spectrum observed at various time intervals after picosecond excitation of colloidal TiO_2. Conditions: $[TiO_2]$ = 17 g/l, pH 2.7, Ar saturated solution, optical pathlength 0.2 cm. Average number of electron-hole pairs present initially in one TiO_2 particle is 67.



In Figure 5 the spectrum of the trapped electron develops within the leading edge of the laser pulse indicating that the trapping time of the electron is less than 40 ps. Subsequently, the electron absorption decays due to recombination with valence band holes.

$$TiO_2(e^-_{tr} + h^+) \xrightarrow{k} TiO_2 \tag{16}$$

where k is expressed in s^{-1} in analogy to the intramicellar processes. We have conceived a stochastic model to analyze the kinetics of this reaction. Since the recombination takes place between a restricted number of charge carriers restricted to the minute reaction space of a 120 Å sized colloidal TiO_2 particle, it cannot be treated by conventional homogeneous solution kinetics. The time differential of the probability that a particle contains x electron-hole pairs at time t is given by:

$$dP_x(t)/dt = k(x+1)^2 P_{x+1}(t) - kx^2 P_x(t) \tag{17}$$

where x = 0,1,2, ... Equation (17) is only valid if the recombination between single electron-hole pairs is a first order event. That this is a valid assumption was shown in the previous paragraphs. This system of differential equations is to be solved subject to the condition that the initial distribution of electron-hole pairs over the particles follows Poisson statistics. The average number of pairs present at time t, $\langle x \rangle (t)$, can be calculated by means of the generating function technique (8, 9) yielding:

$$\langle x\rangle (t) = \sum_{n=1}^{\infty} c_n \exp(-n^2kt) \tag{18}$$

where

$$c_n = 2\exp(-\langle x\rangle_o)\,(-1)^n\, n \sum_{i=n}^{\infty} \frac{\langle x\rangle_o^{\,i}}{(n+i)!} \prod_{j=1}^{n} (n-i-j) \tag{19}$$

The parameter $\langle x\rangle_o$ is the average number of pairs present at t = 0.

Two limiting cases of equation (18) are particularly relevant: when $\langle x\rangle_o$ is very small, equation (18) becomes a simple exponential and the electron-hole recombination follows a first order rate law. Conversely, at high average initial occupancy of the semiconductor particles by electron-hole pairs, i.e. $\langle x\rangle_o > 30$, equation (18) approximates to a second order rate equation.

$$\langle x\rangle (t) = \frac{\langle x\rangle_o}{1+\langle x\rangle_o\, kt} \tag{20}$$

In Figure 3 the initial concentration of electron-hole pairs was sufficiently high to allow for evaluation of the recombination process by the second order rate equation, equation (20). The analysis gives for k_1 the value $3 \times 10^7 s^{-1}$ corresponding to a lifetime of ca. 30 ns for a single electron-hole pair in a colloidal TiO_2 particle. Multiplication of k_1 with the volume of the TiO_2 particles, which is $9 \times 10^{-19} cm^{-3}$, gives the second order rate coefficient $k_2 = 3.0 \times 10^{-11} cm^3 s^{-1}$, as expressed in the conventional units $R_2 = 1.8 \times 10^{10} M^{-1} s^{-1}$.

CONCLUSIONS

Chemical reactivity can be controlled by organised assemblies that act as hosts for the reactant molecules. We have given here a few examples which illustrate the effects of reactant confinement on simple biomolecular processes. It is shown that the kinetic equations established for homogeneous media are no longer applicable if the reactants are sequestered in a reaction space of minute dimensions. New rate laws are derived which are adequate for the description of such processes. Moreover the interaction of reactive species in confined space is simulated by Monte Carlo calculations. We have restricted the scope of the present discussion to a few illustrative examples from our own research. Similar situations are encountered in a variety of other systems, such as the time evolution of products in solid state photochemical reactions.[11]

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