Theory of Diffusion-Influenced Radical Recombination: Interplay between Geminate and Bulk Recombination

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We have formulated a theory for describing the time-dependent rate of the photolytic radical recombination reaction occuring in a viscous medium. The recombination after flash photolysis consists of an initial geminate-pair recombination phase followed by a slower bulk recombination phase in which radicals from different parent molecules encounter *via* diffusion and combine. In most theories of photolytic radical recombination reactions, however, only the dynamics of a single geminate pair was considered and the intervention of surrounding radicals in the geminate pair dynamics was neglected. The present theory treats the interplay of the geminate-pair and the bulk recombinations within a unified framework. Numerical calculations show that prediction of the present theory differs significantly from that of conventional theories.

Introduction

A few years ago Lee and Karplus[1] proposed a general theory of diffusion-influenced reactions, which is based on a hierarchical system of many-body Smoluchowski equations for the reactant molecule distribution functions. There, in treating reactions of the type

$$A+B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C \tag{1.1}$$

we have assumed that thermal dissociation rate of C molecules is comparable to the combination rate of A and B molecules. Hence, initially we have nonnegligible concentration of A and B molecules.

However, in the case of photolytic radical recombination reactions, the initial concentrations of A and B molecules may be practically zero before the onset of photodissociation and the dissociation rate coefficient k_r should include both thermal and photolytic contributions. To treat such cases we have to extend the previous formalism.

There are three issues that will be addressed in the present work. First, in most theories of photolytic radical recombination reactions[2-10], only the dynamics of a single geminate pair was considered and the intervention of other radicals in the geminate pair dynamics was neglected. Hence a unified theory to deal with both the geminate recombination phase and the onset of bulk recombination phase (*i.e.*, when the nongeminate recombination dominates) must be pursued especially to understand the intermediate to long time reaction dynamics. Recently, there have been a few attempts[11-14] to deal with this aspect of photolytic radical recombination reactions. However, the treatments involved some unappealing aspects from physical viewpoints. For example, validity of the theory of Agmon and Szabo[14] is limited to the pseudo-first-order case, namely where one reactant, say B, is present in excess over the other, say A. Furthermore, their theory involves an assumption that the geminate and bulk bimolecular rebindings are independent, which is not true in general.

Second, in all previous theoretical treatments of photolytic radical recombination reactions[2-14], it has been assumed that all radicals are produced at $t=0$ by a δ-function-like light pulse. But the photolysis pulses employed in experiments may not be very much shorter than the recombination times so that some convolution of the δ-function pulse result and the time profile of light pulse is necessitated to compare the theoretical prediction with experimental results. An implicit assumption in such approaches is that newly generated radical pairs will be in the same dynamic environment on the average. This assumption may be appropriate if the external photolytic radiation is so weak that its perturbations on the radical population and distribution are very small. But the assumption fails when the radical concentrations accumulate considerably under a photolysis pulse with long duration. A similar situation has been discussed recently in the case of diffusion-influenced fluorescence quenching[15]. In the present theory, we consider explicitly a photolysis pulse of finite duration from the beginning.

Third, in most theories of photolytic radical recombination reactions, contribution from concurrent generation of radicals by thermal dissociation was neglected. We find that in some cases as examined below this contribution should not be neglected especially in the analysis of intermediate to long time kinetic data of photolytic experiments.

In the present work, we extend the previous formalism[1] for treating reversible diffusion-influenced reactions to incorporate the above-mentioned aspects in the photolytic radical recombination reactions. The paper is organized as follows. In section 2 we present a general theoretical framework for describing the radical recombination dynamics following photodissociation. In section 3 we obtain a formal expression for the time-dependent recombination rate coefficient and evaluate it analytically for a simple case in which the potential of mean force and the hydrodynamic interaction between the radicals may be neglected. In section 4 we then explore the implications of the present theory, in contrast to the conventional theory, *via* the numerical calculation of the variation of the radical concentration with time.

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Kinetic equations

Suppose that there are N_A^0 molecules of species A and N_B^0 molecules of species B. These numbers include the bound ones in C molecules. We than label molecules of species A and B as A_i $(i=1,2,\cdots,N_A^0)$ and B_j $(j=1,2,\cdots,N_B^0)$, respectively, and introduce the following probability density funtions:

$P_{A_i}(\mathbf{r}_A,t)$= probability density that the molecule A_i is in the unbound state and is located at $\mathbf{r}_A$ at time t;
$P_{B_j}(\mathbf{r}_B,t)$= probability density that the molecule B_j is in the unbound state and is located at $\mathbf{r}_B$ at time t;
$P_{A_iB_j}(\mathbf{r}_A,\mathbf{r}_B,t)$= probability density that both A_i and B_j are in the unbound state and are located at $\mathbf{r}_A$ and $\mathbf{r}_B$, respectively, at time t;
$P_{C_{ij}}(\mathbf{r}_C,\boldsymbol{\Omega}_C,t)$= probability density that at time t A_i and B_j form a bound molecule C that is located at $\mathbf{r}_C$ with orientation $\boldsymbol{\Omega}_C$;
$P_{A_iA_lB_j}(\mathbf{r}_A,\mathbf{r}_A',\mathbf{r}_B,t)$= probability density that at time t A_i, A_l and B_j are in the unbound state and are located at $\mathbf{r}_A$, $\mathbf{r}_A'$ and $\mathbf{r}_B$, respectively;
$P_{A_iC_{lj}}(\mathbf{r}_A,\mathbf{r}_C,\boldsymbol{\Omega}_C,t)$= probability density that at time t A_i in the unbound state is located at $\mathbf{r}_A$ and A_l and B_j form a bound molecule C located at $\mathbf{r}_C$ with orientation $\boldsymbol{\Omega}_C$;

and so on. As the notation implies, we are neglecting any orientational anisotropy in molecules A and B. This neglect may be justified if the molecules are small and have spherical shapes so that their reorientational motion occurs very rapidly compared to the diffuisive translational motion.

The evolutions of the one-particle probability density funtions P_{A_i} and P_{B_j} are governed by the following kinetic equations[1]:

$$\frac{\partial}{\partial t}P_{A_i}(\mathbf{r}_A,t)=L_A P_{A_i}(\mathbf{r}_A,t)-\sum_{j=1}^{N_B^0}\int d\mathbf{r}_B d\mathbf{Z}_C\ S_{AB}^C(\mathbf{r}_A,\mathbf{r}_B|\mathbf{Z}_C)\times P_{A_iB_j}(\mathbf{r}_A,\mathbf{r}_B,t)+\sum_{j=1}^{N_B^0}\int d\mathbf{r}_B d\mathbf{Z}_C\ S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A,\mathbf{r}_B;t)P_{C_{ij}}(\mathbf{Z}_C,t) \tag{1}$$

$$\frac{\partial}{\partial t}P_{B_j}(\mathbf{r}_B,t)=L_B P_{B_j}(\mathbf{r}_B,t)-\sum_{i=1}^{N_A^0}\int d\mathbf{r}_A d\mathbf{Z}_C\ S_{AB}^C(\mathbf{r}_A,\mathbf{r}_B|\mathbf{Z}_C)\times P_{A_iB_j}(\mathbf{r}_A,\mathbf{r}_B,t)+\sum_{i=1}^{N_A^0}\int d\mathbf{r}_A d\mathbf{Z}_C\ S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A,\mathbf{r}_B;t)P_{C_{ij}}(\mathbf{Z}_C,t) \tag{2}$$

Each term on the right hand sides of eqs. (1) and (2) has the following physical meaning. L_A (L_B) is the Smoluchowski operater governing the thermal evolution of the one-particle probability density funtion P_{A_i} (P_{B_j}) in the absence of reaction. The sink function $S_{AB}^C(\mathbf{r}_A,\mathbf{r}_B|\mathbf{Z}_C)$ represents the depopulation rate of the unbound molecules A and B at $\mathbf{r}_A$ and $\mathbf{r}_B$ due to the formation of a bound molecule C with configuration $\mathbf{Z}_C\equiv(\mathbf{r}_C,\boldsymbol{\Omega}_C)$. The sink function $S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A,\mathbf{r}_B;t)$ represents the dissociation rate of a complex molecule C with configuration $\mathbf{Z}_C$ into unbound molecules A and B at $\mathbf{r}_A$ and $\mathbf{r}_B$. We will assume that these sink functions can be represented by

$$S_{AB}^C(\mathbf{r}_A,\mathbf{r}_B|\mathbf{Z}_C)=k_i^f\ \delta(\mathbf{r}_C-\mathbf{R})\delta(\cos\beta_C-\cos\beta_r)\delta(\alpha_C-\alpha_r)\delta(r_{BA}-\sigma)/\sigma^2 \tag{3}$$

$$S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A,\mathbf{r}_B;t)=k_i^r\ \delta(\mathbf{r}_C-\mathbf{R})\delta(\cos\beta_C-\cos\beta_r)\delta(\alpha_C-\alpha_r)\delta(r_{BA}-\sigma)/\sigma^2 +k_p(t)\ \delta(\mathbf{r}_C-\mathbf{R})\delta(\cos\beta_C-\cos\beta_r)\delta(\alpha_C-\alpha_r)\delta(r_{BA}-\sigma_d)/\sigma_d^2 \tag{4}$$

where $(r_{BA},\beta_r,\alpha_r)$ are the spherical polar coordinates of $\mathbf{r}_{BA}$ $(=\mathbf{r}_B-\mathbf{r}_A)$, and $\mathbf{R}$ is the center-of-mass coordinates of the unbound A-B pair. (β_C,α_C) $(=\boldsymbol{\Omega}_C)$ are the angles representing the orientation of the C molecule formed from the A-B pair. k_i^f in eq. (3) is the parameter measuring the recombination rate of the A-B pair at the separation of $r_{BA}=\sigma$. In eq. (4), the first term on the right hand side represents the contribution from thermal dissociation of C, while the second term that from photodissociation. As denoted, the separation of a photodissociated A-B radical pair is σ_d which may be different from the separation σ of a thermally dissociated pair[16]. In general we have $\sigma_d\geq\sigma$. While k_i^r is a constant, $k_p(t)$ and thus S_C^{AB} may vary in time since the photodissociation rate depends on the radiation intensity.

Similarly, the evolution of the probability density funtion $P_{C_{ij}}$ is governed by

$$\frac{\partial}{\partial t}P_{C_{ij}}(\mathbf{Z}_C,t)=L_C P_{C_{ij}}(\mathbf{Z}_C,t)-\int d\mathbf{r}_A d\mathbf{r}_B\ S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A,\mathbf{r}_B;t)\ P_{C_{ij}}(\mathbf{Z}_C,t)+\int d\mathbf{r}_A d\mathbf{r}_B\ S_{AB}^C(\mathbf{r}_A,\mathbf{r}_B|\mathbf{Z}_C)\ P_{A_iB_j}(\mathbf{r}_A,\mathbf{r}_B,t) \tag{5}$$

The two-particle probability density function $P_{A_iB_j}$ evolves in turn according to

$$\begin{aligned}\frac{\partial}{\partial t}P_{A_iB_j}(\mathbf{r}_A,\mathbf{r}_B,t)=&L_{AB}\ P_{A_iB_j}(\mathbf{r}_A,\mathbf{r}_B,t)\\&-\int d\mathbf{Z}_C\ S_{AB}^C(\mathbf{r}_A,\mathbf{r}_B|\mathbf{Z}_C)\ P_{A_iB_j}(\mathbf{r}_A,\mathbf{r}_B,t)\\&+\int d\mathbf{Z}_C\ S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A,\mathbf{r}_B;t)P_{C_{ij}}(\mathbf{Z}_C,t)\\&-\sum_{\substack{l=1\\l\neq i}}^{N_A^0}\int d\mathbf{r}_A'd\mathbf{Z}_C\ S_{AB}^C(\mathbf{r}_A',\mathbf{r}_B|\mathbf{Z}_C)\ P_{A_lA_iB_j}(\mathbf{r}_A,\mathbf{r}_A',\mathbf{r}_B,t)\\&-\sum_{\substack{k=1\\k\neq j}}^{N_B^0}\int d\mathbf{r}_B'd\mathbf{Z}_C\ S_{AB}^C(\mathbf{r}_A,\mathbf{r}_B'|\mathbf{Z}_C)\ P_{A_iB_jB_k}(\mathbf{r}_A,\mathbf{r}_B,\mathbf{r}_B',t)\\&+\sum_{\substack{l=1\\l\neq i}}^{N_A^0}\int d\mathbf{Z}_C d\mathbf{r}_A'\ S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A',\mathbf{r}_B;t)\ P_{A_iC_{lj}}(\mathbf{r}_A,\mathbf{Z}_C,t)\\&+\sum_{\substack{k=1\\k\neq j}}^{N_B^0}\int d\mathbf{Z}_C d\mathbf{r}_B'\ S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A,\mathbf{r}_B';t)\ P_{B_jC_{ik}}(\mathbf{r}_B,\mathbf{Z}_C,t)\end{aligned} \tag{6}$$

Here L_{AB} is the Smoluchowski operator governing the evolution of the two-particle probability density function $P_{A_iB_j}$ in the absence of reaction. The second and the third terms represent the disappearance and regeneration of the A_i-B_j pair due to formation and dissociation of the complex molecule C_{ij}, respectively. The fourth and fifth terms involving the three-particle probability density functions account for the removal of either A_i or B_j due to the competitive reaction with a third molecule other than A_i and B_j. On the other hand, the sixth and the seventh terms represent the changes due to the recovery of either A_i or B_j by the dissociation of a complex molecule formed with a third molecule.

Higher order equations governing many-particle probability density functions can be written down in a straightforward manner, but the solution to the whole hierarchy of kinetic equations is difficult to obtain. To truncate the hierarchy at the level of two-particle kinetic equations, we need to approximate the three-particle probability density functions in terms of one-particle and two-particle probability density functions. In the superposition approximation[1,17,18], we may write

$$P_{A_iA_lB_j}(\mathbf{r}_A,\mathbf{r}_A',\mathbf{r}_B,t)\cong P_{B_j}(\mathbf{r}_B,t)\ P_{A_i(B_j)}(\mathbf{r}_A,t|\mathbf{r}_B)\ P_{A_l(B_j)}(\mathbf{r}_A',t|\mathbf{r}_B) \tag{7}$$

Here $P_{A_i(B_j)}(\mathbf{r}_A,t|\mathbf{r}_B)$ denotes the conditional probability density that A_i is at $\mathbf{r}_A$ at time t given that B_j is at $\mathbf{r}_B$. $P_{A_l(B_j)}(\mathbf{r}_A',t|\mathbf{r}_B)$ is defined similarly. In passing we note that in terms of this conditional probability density the two-particle probability density function can be expressed exactly as

$$P_{A_iB_j}(\mathbf{r}_A,\mathbf{r}_B,t)=P_{B_j}(\mathbf{r}_B,t)\ P_{A_i(B_j)}(\mathbf{r}_A,t|\mathbf{r}_B)=P_{A_i}(\mathbf{r}_A,t)\ P_{B_j(A_i)}(\mathbf{r}_B,t|\mathbf{r}_A) \tag{8}$$

We then introduce various concentration (number density) fields that are related to the particle distribution functions as follows:

$$C_A(\mathbf{r}_A,t)=\text{the number density of } A \text{ molecules at } \mathbf{r}_A \text{ at time } t$$
$$=\sum_{i=1}^{N_A^0} P_{A_i}(\mathbf{r}_A,t) \tag{9}$$

$$C_B(\mathbf{r}_B,t)=\text{the number density of } B \text{ molecules at } \mathbf{r}_B \text{ at time } t$$
$$=\sum_{j=1}^{N_B^0} P_{B_j}(\mathbf{r}_B,t) \tag{10}$$

$$\Phi_C(\mathbf{Z}_C,t)=\text{the number density of } C \text{ molecules with orientation } \mathbf{\Omega}_C \text{ at } \mathbf{r}_A \text{ at time } t$$
$$=\sum_{i=1}^{N_A^0}\sum_{j=1}^{N_B^0} P_{C_{ij}}(\mathbf{Z}_C,t) \tag{11}$$

$$C_{A(B_j)}(\mathbf{r}_A,t|\mathbf{r}_B)=\text{the number density of } A \text{ molecules at } \mathbf{r}_A \text{ at time } t \text{ given that } B_j \text{ is at } \mathbf{r}_B$$
$$=\sum_{i=1}^{N_A^0} P_{A_i(B_j)}(\mathbf{r}_A,t|\mathbf{r}_B) \tag{12}$$

and so on. Kinetic equations governing the evolution of these concentration fields may be obtained by summing eqs. (1), (2), (5) and (6) for all reactant molecules. We make the usual assumptions that (i) the volume V of reaction vessel is large enough and the shape is such that surface effects may be neglected, (ii) the initial distribution of reactant molecules is an equilibrium one except for a specific correlation between each geminate pair of A and B molecules, and (iii) there is no external field. We will then have

$$C_A(\mathbf{r}_A,t)=[A];\ C_B(\mathbf{r}_B,t)=[B];\ \Phi_C(\mathbf{Z}_C,t)=[C]/4\pi \tag{13}$$

where $[\alpha]$ denotes the uniform bulk concentration of species α at time t. Also with such experimental conditions, the conditional concentration fields, $C_{A(B_j)}$'s, are statistically equivalent for all j and depend only on the relative separation $|\mathbf{r}_B-\mathbf{r}_A|$; that is,

$$C_{A(B_j)}(\mathbf{r}_A,t|\mathbf{r}_B)=C_{A(B)}(r_{BA},t)=[A]\ \rho_{AB}(r_{BA},t) \tag{14}$$

where we have also introduced the nonequilibrium pair correlation function $\rho_{AB}(r_{BA},t)$ which characterizes the relative distribution between unbound A and B molecules at time t.

With these assumptions, summing eq. (1) over $i=1,2,\cdots,N_A^0$ yields

$$\frac{\partial}{\partial t}[A]=L_A\ [A]-\int d\mathbf{r}_B d\mathbf{Z}_C\ S_{AB}^{C}(\mathbf{r}_A,\mathbf{r}_B|\mathbf{Z}_C)\rho_{AB}(r_{BA},t)[A][B]$$
$$+\frac{1}{4\pi}\int d\mathbf{Z}_C d\mathbf{r}_B\ S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A,\mathbf{r}_B;t)[C] \tag{15}$$

Since $L_A=D_A\ \nabla_A^2$, where D_A is the diffusion coefficient of A, and $[A]$ is independent of $\mathbf{r}_A$, the first term on the right hand side drops out and eq. (15) reduces to the familiar rate law,

$$\frac{d}{dt}[A]=-k_f(t)[A][B]+k_r(t)[C] \tag{16}$$

Here the ***time-dependent*** bimolecular recombination rate coefficient $k_f(t)$ and the unimolecular dissociation rate coefficient $k_r(t)$ are defined by

$$k_f(t)=\int d\mathbf{r}_B d\mathbf{Z}_C\ S_{AB}^{C}(\mathbf{r}_A,\mathbf{r}_B|\mathbf{Z}_C)\rho_{AB}(r_{BA},t)$$
$$=4\pi k_i^f\ \rho_{AB}(\sigma,t) \tag{17}$$

$$k_r(t)=\frac{1}{4\pi}\int d\mathbf{Z}_C d\mathbf{r}_B\ S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A,\mathbf{r}_B;t)$$
$$=k_i^r+k_p(t) \tag{18}$$

In the absence of external radiation, we have

$$k_r(t)=k_i^r=k_{eq}^r \tag{19}$$

which identifies the thermal dissociation rate parameter k_i^r as the equilibrium rate constant for $C\rightarrow A+B$ reaction. Summing eq. (2) over j or summing eq. (5) over i and j gives the same rate equation as eq. (16):

$$\frac{d}{dt}[B]=-\frac{d}{dt}[C]=-k_f(t)[A][B]+k_r(t)[C] \tag{20}$$

To evaluate the bimolecular rate coefficient $k_f(t)$, we need an explicit expression for the noneqlilibrium pair-correlation function ρ_{AB}. The kinetic equation governing the evolution of ρ_{AB} is in turn obtained from eq. (6). Summing eq. (6) over i and j gives

$$\frac{\partial}{\partial t}\{[A][B]\rho_{AB}(r_{BA},t)\}=[A][B]\ L_{AB}\rho_{AB}(r_{BA},t)$$
$$-\int d\mathbf{Z}_C\ S_{AB}^{C}(\mathbf{r}_A,\mathbf{r}_B|\mathbf{Z}_C)\rho_{AB}(r_{BA},t)\ [A][B]$$
$$+\frac{1}{4\pi}\int d\mathbf{Z}_C\ S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A,\mathbf{r}_B;t)\ [C]$$
$$-\int d\mathbf{r}_A' d\mathbf{Z}_C\ S_{AB}^{C}(\mathbf{r}_A',\mathbf{r}_B|\mathbf{Z}_C)\ \sum_{i=1}^{N_A^0}\ \sum_{j=1}^{N_B^0}\ \sum_{\substack{l=1\\ l\neq i}}^{N_A^0} P_{A_iA_lB_j}(\mathbf{r}_A,\mathbf{r}_A',\mathbf{r}_B,t)$$
$$-\int d\mathbf{r}_B' d\mathbf{Z}_C\ S_{AB}^{C}(\mathbf{r}_A,\mathbf{r}_B'|\mathbf{Z}_C)\ \sum_{i=1}^{N_A^0}\ \sum_{j=1}^{N_B^0}\ \sum_{\substack{k=1\\ k\neq j}}^{N_B^0} P_{A_iB_jB_k}(\mathbf{r}_A,\mathbf{r}_B,\mathbf{r}_B',t)$$
$$+\int d\mathbf{Z}_C d\mathbf{r}_A'\ S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A',\mathbf{r}_B;t)\ \sum_{i=1}^{N_A^0}\ \sum_{j=1}^{N_B^0}\ \sum_{\substack{l=1\\ l\neq i}}^{N_A^0} P_{A_iC_{lj}}(\mathbf{r}_A,\mathbf{Z}_C,t)$$
$$+\int d\mathbf{Z}_C d\mathbf{r}_B'\ S_C^{AB}(\mathbf{Z}_C|\mathbf{r}_A,\mathbf{r}_B';t)\ \sum_{i=1}^{N_A^0}\ \sum_{j=1}^{N_B^0}\ \sum_{\substack{k=1\\ k\neq j}}^{N_B^0} P_{B_jC_{ik}}(\mathbf{r}_B,\mathbf{Z}_C,t) \tag{21}$$

Terms involving the triple summation of three-particle probability density functions can be manipulated by using the superposition approximation eq. (7). For example, we have

$$\begin{aligned}\sum_{i=1}^{N_A^0}\sum_{j=1}^{N_B^0}\sum_{\substack{l=1\\ l\neq i}}^{N_A^0} & P_{A_iA_l B_j}(\boldsymbol{r}_A,\boldsymbol{r}_A',\boldsymbol{r}_B,t)\\ &\cong \sum_{j=1}^{N_B^0} P_{B_j}(\boldsymbol{r}_B,t)\sum_{i=1}^{N_A^0} P_{A_i(B_j)}(\boldsymbol{r}_A,t|\boldsymbol{r}_B)\sum_{l=1}^{N_A^0} P_{A_l(B_j)}(\boldsymbol{r}_A',t|\boldsymbol{r}_B)\\ &\quad-\sum_{j=1}^{N_B^0} P_{B_j}(\boldsymbol{r}_B,t)\sum_{i=1}^{N_A^0} P_{A_i(B_j)}(\boldsymbol{r}_A,t|\boldsymbol{r}_B)P_{A_i(B_j)}(\boldsymbol{r}_A',t|\boldsymbol{r}_B)\\ &=[B]\ C_{A(B)}(r_{BA},t)\ C_{A(B)}(r_{BA}',t)+O\Big(\frac{[A][B]}{V}\Big)\\ &\cong[B][A]^2\ \rho_{AB}(r_{BA},t)\ \rho_{AB}(r_{AB}',t)\end{aligned}\tag{22}$$

where $r_{BA}=|\boldsymbol{r}_A-\boldsymbol{r}_B|$ and $r_{BA}'=|\boldsymbol{r}_A'-\boldsymbol{r}_B|$. The term denoted by $O([A][B]/V)$ has the magnitude comparable to $[A][B]/V$ and can be neglected in the $V\rightarrow\infty$ limit. A similar manipulation gives

$$\sum_{i=1}^{N_A^0}\sum_{j=1}^{N_B^0}\sum_{\substack{k=1\\ k\neq j}}^{N_B^0} P_{A_iB_jB_k}(\boldsymbol{r}_A,\boldsymbol{r}_B,\boldsymbol{r}_B',t)\cong[A][B]^2\ \rho_{AB}(r_{BA},t)\ \rho_{AB}(r_{BA}'',t)\tag{23}$$

where $r_{BA}''=|\boldsymbol{r}_A-\boldsymbol{r}_B'|$. The triple summations in the 6th and the 7th terms on the right hand side of eq. (21) can be in turn manipulated as

$$\begin{aligned}\sum_{i=1}^{N_A^0}\sum_{j=1}^{N_B^0}\sum_{\substack{l=1\\ l\neq i}}^{N_A^0} & P_{A_iC_{lj}}(\boldsymbol{r}_A,\boldsymbol{Z}_C,t)\\ &=\sum_{j=1}^{N_B^0}\sum_{\substack{l=1\\ l\neq i}}^{N_A^0} P_{C_{lj}}(\boldsymbol{Z}_C,t)\sum_{i=1}^{N_A^0} P_{A_i(C_{lj})}(\boldsymbol{r}_A,t|\boldsymbol{Z}_C)\\ &=\sum_{j=1}^{N_B^0}\sum_{\substack{l=1\\ l\neq i}}^{N_A^0} P_{C_{lj}}(\boldsymbol{Z}_C,t)\ [A]\ \rho_{AC}(\boldsymbol{r}_A,t|\boldsymbol{Z}_C)\\ &\cong\Phi_C(\boldsymbol{Z}_C,t)\ [A]\ \rho_{AC}(\boldsymbol{r}_A,t|\boldsymbol{Z}_C)\\ &=\frac{1}{4\pi}[C][A]\ \rho_{AC}(\boldsymbol{r}_A,t|\boldsymbol{Z}_C)\end{aligned}\tag{24}$$

and

$$\sum_{i=1}^{N_A^0}\sum_{j=1}^{N_B^0}\sum_{\substack{k=1\\ k\neq j}}^{N_B^0} P_{B_jC_{ik}}(\boldsymbol{r}_B,\boldsymbol{Z}_C,t)\cong\frac{1}{4\pi}[C][B]\ \rho_{BC}(\boldsymbol{r}_B,t|\boldsymbol{Z}_C)\tag{25}$$

Here $P_{A_i(C_{lj})}(\boldsymbol{r}_A,t|\boldsymbol{Z}_C)$ denotes the conditional probability density that A_i is at $\boldsymbol{r}_A$ at time t given that C_{lj} is at the configuration $\boldsymbol{Z}_C$. $\rho_{AC}(\boldsymbol{r}_A,t|\boldsymbol{Z}_C)$ is the nonequilibrium pair correlation function between A and C molecules; that is, $[A]\rho_{AC}(\boldsymbol{r}_A,t|\boldsymbol{Z}_C)$ gives the number density of A molecules at $\boldsymbol{r}_A$ given that a C molecules is at the configuration $\boldsymbol{Z}_C$. $\rho_{BC}(\boldsymbol{r}_B,t|\boldsymbol{Z}_C)$ is defined similarly.

Substituting eqs. (22)-(25) into eq. (21) and using the rate law given by eq. (16) together with eqs. (17) and (18) defining the rate coefficients $k_f(t)$ and $k_r(t)$, we obtain

$$\begin{aligned}[A][B]\frac{\partial}{\partial t}\rho_{AB}(r_{BA},t)&=[A][B]\ L_{AB}\rho_{AB}(r_{BA},t)\\ &\quad-[A][B]\ k_i^f\frac{\delta(r_{BA}-\sigma)}{\sigma^2}\rho_{AB}(r_{BA},t)\\ &\quad+k_i^r\frac{\delta(r_{BA}-\sigma)}{4\pi\sigma^2}[C]+k_p(t)\frac{\delta(r_{BA}-\sigma_d)}{4\pi\sigma_d{}^2}[C]\\ &\quad+k_r(t)[A][C]\ \{\rho_{AC}(\boldsymbol{r}_A,t|\boldsymbol{Z}_C)-\rho_{AB}(r_{BA},t)\}\\ &\quad+k_r(t)[B][C]\ \{\rho_{BC}(\boldsymbol{r}_B,t|\boldsymbol{Z}_C)-\rho_{AB}(r_{BA},t)\}\end{aligned}\tag{26}$$

The experimental situation we address in this work is as follows. For $t\leq0$, the system is in the thermodynamic equilibrium state. Although there may be a case in which the equilibrium constant for the combination reaction is so large that $[A]=[B]\cong0$, we can define the equilibrium pair distribution function $g_{AB}^{(2)}(r_{BA})$ between A and B molecules in any cases. Hence we have

$$\rho_{AB}(r_{BA},t)=g_{AB}^{(2)}(r_{BA})\qquad\text{for } t\leq0;\tag{27}$$

$$\frac{\partial}{\partial t}\rho_{AB}(r_{BA},t)=0\qquad\text{for } t\leq0.\tag{28}$$

For $t>0$, the system is irradiated and C molecules begin to dissociate to give appreciable ammounts of $[A]$ and $[B]$. We can then divide eq. (26) by $[A][B]$ to obtain

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{AB}(r_{BA},t)&=L_{AB}\rho_{AB}(r_{BA},t)-k_i^f\frac{\delta(r_{BA}-\sigma)}{\sigma^2}\rho_{AB}(r_{BA},t)\\ &\quad+k_i^r\ \phi(t)\frac{\delta(r_{BA}-\sigma)}{4\pi\sigma^2}+k_p(t)\ \phi(t)\frac{\delta(r_{BA}-\sigma_d)}{4\pi\sigma_d^2}\\ &\quad+k_r(t)\ \phi(t)\ [A]\ \{\rho_{AC}(\boldsymbol{r}_A,t|\boldsymbol{Z}_C)-\rho_{AB}(r_{BA},t)\}\\ &\quad+k_r(t)\ \phi(t)\ [B]\ \{\rho_{BC}(\boldsymbol{r}_B,t|\boldsymbol{Z}_C)-\rho_{AB}(r_{BA},t)\}\end{aligned}\tag{29}$$

where

$$\phi(t)=[C]/[A][B].\tag{30}$$

Expression for the Rate Coefficient $k_f(t)$

When $[A]$ and $[B]$ is not too large, we may neglect the 5th and 6th terms on the right hand side of eq. (29)[1]. Then the equations we have to consider are

$$k_f(t)=4\pi k_i^f\ \rho(\sigma,t)\tag{31}$$

$$\begin{aligned}\frac{\partial}{\partial t}\rho(r,t)&=L_0(r)\rho(r,t)-S(r)\rho(r,t)\\ &\quad+k_i^r\phi(t)\frac{\delta(r-\sigma)}{4\pi\sigma^2}+k_p(t)\phi(t)\frac{\delta(r-\sigma_d)}{4\pi\sigma_d^2}\qquad(t>0)\end{aligned}\tag{32}$$

To simplify the notation we have left out the subscripts AB and BA from ρ_{AB} and $r_{BA}(=|\boldsymbol{r}_B-\boldsymbol{r}_A|)$, respectively, and have introduced

$$S(r)=\int d\boldsymbol{Z}_C\ S_{AB}^C(\boldsymbol{r}_A,\boldsymbol{r}_B|\boldsymbol{Z}_C)=k_i^f\frac{\delta(r-\sigma)}{\sigma^2}\tag{33}$$

$L_0(r)$ is the reduced Smoluchowski operator[1] for the relative motion of A and B, and is given by

$$L_0(r)=\Big(\frac{\partial}{\partial r}+\frac{2}{r}\Big)d(r)\Big[\frac{\partial}{\partial r}+\beta\frac{\partial}{\partial r}U(r)\Big]\tag{34}$$

where $d(r)$ denotes the relative diffusion coefficient, which depends on r if the hydrodynamic interaction between A and B is to be included, and $U(r)$ is the potential of mean force. $\beta=1/k_BT$ with the Boltzmann constant k_B and the absolute temperature T.

If $U(r)$ has a very steep potential wall at $r=\sigma$, $\rho(r,t)$ must satisfy the reflecting boundary condition,

$$\left\{d(r)\left[\frac{\partial}{\partial r}+\beta\frac{\partial}{\partial r}U(r)\right]\rho(r,t)\right\}_{r=\sigma}=0 \tag{35}$$

By the definition given by eq. (14) $\rho(r,t)$ approaches unity as r goes to infinity,

$$\lim_{r\to\infty}\rho(r,t)=1 \tag{36}$$

The initial condition for $\rho(r,t)$ is that given by eq. (27); that is,

$$\rho(r,t=0)=g^{(2)}(r)=\exp[-\beta U(r)] \tag{37}$$

where we omit the subscript AB also from $g^{(2)}_{AB}(r)$.

A formal solution to eq. (32) is given by

$$\rho(r,t)=e^{t[L_0(r)-S(r)]}\rho(r,0)+\int_0^t d\tau\ e^{\tau[L_0(r)-S(r)]}\phi(t-\tau)\left\{k^r_i\frac{\delta(r-\sigma)}{4\pi\sigma^2}+k_b(t-\tau)\frac{\delta(r-\sigma_d)}{4\pi\sigma_d^2}\right\} \tag{38}$$

Using the operator identity[19], eq. (39a),

$$e^{t(A+B)}=e^{tA}+\int_0^t d\tau\ e^{\tau(A+B)}\ B\,e^{(t-\tau)A} \tag{39a}$$

$$=e^{tA}+\int_0^t d\tau\ e^{(t-\tau)A}\ B\,e^{\tau(A+B)} \tag{39b}$$

and noting that $L_0(r)\rho(r,0)=L_0(r)g^{(2)}(r)=0$, we can rewrite the first term on the right hand side of eq. (38) as

$$e^{t[L_0(r)-S(r)]}\rho(r,0)=g^{(2)}(r)-\int_0^t d\tau\ e^{\tau[L_0(r)-S(r)]}S(r)g^{(2)}(r) \tag{40}$$

Putting eq. (38) and (40) into eq. (31), we obtain a formal expression for the rate coefficient $k_f(t)$:

$$\begin{aligned}k_f(t)&=4\pi k^f_i\ \rho(\sigma,t)\\&=\int d\mathbf{r}\ S(r)\rho(r,t)\\&=k^f_{eq}-(k^f_{eq})^2\int_0^t d\tau[1-K_{eq}^{-1}\phi(t-\tau)]\Delta(\tau)\\&\quad+(k^f_{eq})^2\int_0^t d\tau\ K_{eq}^{-1}\phi(t-\tau)\alpha(t-\tau)\Delta_f(\tau)\end{aligned} \tag{41}$$

Here k^f_{eq} is the recombination rate constant that would be observed if the pair distribution between A and B were maintained at equilibrium, and is given by

$$k^f_{eq}=4\pi k^f_i\ g^{(2)}(\sigma) \tag{42}$$

K_{eq} is the equilibrium constant,

$$K_{eq}=k^f_{eq}/k^r_{eq} \tag{43}$$

where $k^r_{eq}=k^r_i$ as noted in eq. (19). The function $\alpha(t)$ is defined by

$$\alpha(t)=k_b(t)/k^r_{eq} \tag{44}$$

$\Delta(\tau)$ and $\Delta_f(\tau)$, which will be called the memory kernels, contain information on the reactive pair dynamics and are represented by the following expressions:

$$\Delta(\tau)=\int d\mathbf{r}\ \mathcal{S}(r)e^{\tau L(r)}\mathcal{S}(r)g^{(2)}(r) \tag{45}$$

$$\Delta_f(\tau)=\int d\mathbf{r}\ \mathcal{S}(r)e^{\tau L(r)}\frac{\delta(r-\sigma_d)}{4\pi\sigma_d^2} \tag{46}$$

where

$$L(r)=L_0(r)-S(r) \tag{47}$$

and

$$\mathcal{S}(r)=S(r)/k^f_{eq}=g^{(2)}(\sigma)^{-1}\frac{\delta(r-\sigma)}{4\pi\sigma^2} \tag{48}$$

We now investigate the structure of the memory kernels. Using the operator identity, eq. (39b), iteratively with $A=L_0$ and $B=-S(r)=-k^f_{eq}\mathcal{S}(r)$, we can write

$$\begin{aligned}\Delta(\tau)=&\int d\mathbf{r}\mathcal{S}(r)e^{\tau L_0(r)}\mathcal{S}(r)g^{(2)}(r)\\&-k^f_{eq}\int d\mathbf{r}\mathcal{S}(r)\int_0^\tau d\tau_1 e^{(\tau-\tau_1)L_0(r)}\mathcal{S}(r)e^{\tau_1 L(r)}\mathcal{S}(r)g^{(2)}(r)\end{aligned} \tag{49}$$

Eqs. (45) and (49) for $\Delta(\tau)$ may be rewritten in the form

$$\begin{aligned}\Delta(\tau)&=\int d\mathbf{r}\mathcal{S}(r)\int d\mathbf{r}_0 e^{\tau L(r)}\left[\frac{\delta(r-r_0)}{4\pi r_0^2}\right]\mathcal{S}(r_0)g^{(2)}(r_0)\\&=\int d\mathbf{r}\mathcal{S}(r)\int d\mathbf{r}_0 e^{\tau L_0(r)}\left[\frac{\delta(r-r_0)}{4\pi r_0^2}\right]\mathcal{S}(r_0)g^{(2)}(r_0)\\&\quad-k^f_{eq}\int_0^\tau d\tau_1\int d\mathbf{r}\mathcal{S}(r)\int d\mathbf{r}_1 e^{(\tau-\tau_1)L_0(r)}\left[\frac{\delta(r-r_1)}{4\pi r_1^2}\right]\mathcal{S}(r_1)\\&\quad\times\int d\mathbf{r}_0 e^{\tau_1 L(r_1)}\left[\frac{\delta(r_1-r_0)}{4\pi r_0^2}\right]\mathcal{S}(r_0)g^{(2)}(r_0)\end{aligned} \tag{50}$$

Introducing the Green's functions for eq. (32) in the presence and in the absence of reaction,

$$G_R(r,t|r_0)=e^{tL(r)}\left[\frac{\delta(r-r_0)}{4\pi r_0^2}\right] \tag{51}$$

$$G(r,t|r_0)=e^{tL_0(r)}\left[\frac{\delta(r-r_0)}{4\pi r_0^2}\right] \tag{52}$$

and performing the space integrations with $\mathcal{S}(r)$ given by eq. (48), we rewrite eq. (50) as

$$\begin{aligned}\Delta(\tau)&=g^{(2)}(\sigma)^{-1}\ G_R(\sigma,\tau|\sigma)\\&=g^{(2)}(\sigma)^{-1}\ G(\sigma,\tau|\sigma)\\&\quad-k^f_{eq}\int_0^\tau d\tau_1[g^{(2)}(\sigma)^{-1}\ G(\sigma,\tau-\tau_1|\sigma)][g^{(2)}(\sigma)^{-1}\ G_R(\sigma,\tau_1|\sigma)]\end{aligned} \tag{53}$$

Taking the Laplace transformation of this equation [the Laplace transform of any function $f(t)$ will be denoted by $\hat{f}(z)$], we obtain

$$\hat{\Delta}(z)=[1+k^f_{eq}\hat{\Delta}_0(z)]^{-1}\ \hat{\Delta}_0(z) \tag{54}$$

where

$$\hat{\Delta}_0(z)=g^{(2)}(\sigma)^{-1}\ \hat{G}(\sigma,z|\sigma) \tag{55}$$

The same procedure can be applied to obtain the expression for $\hat{\Delta}_f(z)$:

$$\hat{\Delta}_f(z)=[1+k^f_{eq}\hat{\Delta}_0(z)]^{-1}\ [g^{(2)}(\sigma)^{-1}\ \hat{G}(\sigma,z|\sigma_d)] \tag{56}$$

Explicit expressions for $\Delta(\tau)$ and $\Delta_f(\tau)$ have been obtained only for a very simple model case. We assume that the potential of mean force $U(r)$ vanishes for $r\geq\sigma$ but goes to infinity for $r<\sigma$. We also assume that the hydrodynamic interaction between A and B is negligible so that $d(r)$ is simply given by the sum of the diffusion constants of molecules A and B; *i.e.*, $d(r)=D_A+D_B\equiv D$. In this simplest case, the Green's function $\hat{G}(r,z|r_0)$ can be readily obtained:

$$\hat{G}(r,z|r_0)=\frac{1}{4\pi Drr_0}\left\{\frac{1}{2\alpha}\left[\exp(-\alpha|r-r_0|)-\exp(-\alpha(r+r_0-2\sigma))\right]+\frac{\sigma}{1+\alpha\sigma}\exp(-\alpha(r+r_0-2\sigma))\right\} \qquad (57)$$

where $\alpha\equiv(z/D)^{1/2}$. Therefore, the expression for $\hat{\Delta}(z)$ in eq. (54) becomes

$$\hat{\Delta}(z)=[(k'_{eq}+k_D)+k_D\sigma(z/D)^{1/2}]^{-1} \qquad (58)$$

where $k_D=4\pi\sigma D$ Inverse Laplace transformation gives

$$\Delta(t)=k_D^{-1}(D^{1/2}/\sigma)[(1/\pi t)^{1/2}-A\ \Omega(At^{1/2})] \qquad (59)$$

where $A\equiv[1+(k'_{eq}/k_D)](D^{1/2}/\sigma)$, and we have defined the function $\Omega(y)$ as

$$\Omega(y)=\exp(y^2)\ \mathrm{erfc}(y) \qquad (60)$$

Applying the same procedure we obtain

$$\hat{\Delta}_f(z)=k_D^{-1}(D^{1/2}/\sigma)(\sigma/\sigma_d)(z^{1/2}+A)^{-1}\ \exp[-(\sigma_d-\sigma)(z/D)^{1/2}] \quad (61)$$

which gives

$$\Delta_f(t)=k_D^{-1}(D^{1/2}/\sigma)(\sigma/\sigma_d)\ \exp(-B^2/4t)\times\left[(1/\pi t)^{1/2}-A\ \Omega\left(\frac{1}{2}Bt^{-1/2}+At^{1/2}\right)\right] \qquad (62)$$

where A is the same constant as given above and $B\equiv(\sigma_d-\sigma)D^{-1/2}$.

Model calculations

We will consider a general situation where an excess of B molecules may be present at $t=0$; that is,

$$[B]_0=C_B+[A]_0 \qquad (63)$$

where C_B is the concentration of free excess B molecules before the photolytic radiation is turned on and the subscript 0 denoting the values at $t=0$. We assume that initially the excess B molecules, *i.e.*, which are not derived from C molecules, are distributed randomly with respect to A molecules.

The initial concentration of A molecules is then given by

$$[A]_0=\frac{1}{2}\left\{\left[\frac{4C_0}{K_{eq}}+\left(C_B+\frac{1}{K_{eq}}\right)^2\right]^{1/2}-\left(C_B+\frac{1}{K_{eq}}\right)\right\} \qquad (64)$$

where C_0 denotes the total concentration of A molecules that are present either in the bound molecules C or as the free molecules; that is,

$$C_0\equiv[A]_0+[C]_0=[A]+[C] \qquad (65)$$

The rate equation (16) governing the time-dependence of the concentration of unbound A molecules can be written in the form

$$\frac{d}{dt}[A]=-k_f(t)[A](C_B+[A])+k_r(t)(C_0-[A]) \qquad (66)$$

Expression for the time-dependent forward rate coefficient $k_f(t)$ is given by eq. (41) with the memory kernels $\Delta(\tau)$ and $\Delta_f(\tau)$ given by eqs. (59) and (62), respectively. The reverse rate coefficient $k_r(t)$ is given by eq. (18) and depends on the radiation intensity. We can therefore investigate the recombination kinetics for a given system once the irradiation function $\alpha(t)$ [see eq. (44)] and the motional and reaction parameters, D, σ, σ_d, k'_{eq} and k'_{eq}, are provided.

In many experiments, the photolytic radiation cannot be represented as a δ-function pulse. Therefore, in the conventional approach one tries to fit the experimental data to the convolution of the δ-function result with the radiation profile [2,16,20]; that is, it is assumed that

$$[A]=[A]_{eq}+\int_0^t d\tau\ k_p(\tau)[C]_\tau\ S_{conv}(t-\tau) \qquad (67)$$

where the first term $[A]_{eq}$ on the right hand side denotes the equilibrium concentration, and the second term the nonequilibrium contribution due to the photolysis; $d\tau k_p(\tau)[C]_\tau$ is the number of A molecules created by photodissociation of C molecules between times τ and $\tau+d\tau$ and $S_{conv}(t-\tau)$ is the survival probability that an A molecule created at time τ has not recombined with any B molecule until time t. A subtle assumption that is made in evaluating $S_{conv}(t-\tau)$ is that A molecules just created are surrounded by an equilibrium distribution of B molecules except for a correlation with the geminate B molecule. This assumption renders the survival probability of A molecules depends only on the time $(t-\tau)$ elapsed since its creation regardless of when they are created. However, as the formulation presented in section 2 shows clearly, this assumption may be invalidated.

It is usually further assumed that the photolytic radiation is not so intense that variation of $[C]$ with time can be negligible; *i.e.*, $[C]_\tau$ in eq. (67) is assumed to remain constant

$$[C]_\tau=C_0-[A]_\tau\cong C_0 \qquad (68)$$

By substituting eq. (68) into eq. (67) with the relation

$$k_p(t)=k'_{eq}\ \alpha(t), \qquad (69)$$

one obtains

$$[A]-[A]_{eq}=C_0k'_{eq}\ \int_0^t d\tau\ \alpha(\tau)\ S_{conv}(t-\tau) \qquad (70)$$

We compare the numerical prediction of eq. (70) with that obtained by numerical integration of eq. (66) written in the form

$$\frac{dY}{dt}=-k_f(t)Y(t)[C_B+C_0Y(t)]+k_r(t)[1-Y(t)] \qquad (71)$$

where $Y(t)=[A]/C_0$. By the mean value theorem we have

$$Y(t_{i+1})=Y(t_i)-(t_{i+1}-t_i)\{k_f(t_i^m)Y(t_i^m)[C_B+C_0Y(t_i^m)]-k_r(t_i^m)[1-Y(t_i^m)]\} \qquad (72)$$

where t_i^m denotes a time between t_i and t_{i+1}. The value of $k_r(t_i^m)$ is assumed to be given by

$$k_r(t_i^m)\cong[k_r(t_i)+k_r(t_{i+1})]/2=k'_{eq}\left\{1+\frac{1}{2}[\alpha(t_i)+\alpha(t_{i+1})]\right\} \qquad (73)$$

The values of $Y(t_i^m)$ and $k_f(t_i^m)$ are determined by a prediction-correction algorithm. We first put

$$Y(t_i^m) \cong Y^{(0)}(t_i^m) = Y(t_i) \tag{74}$$

and

$$k_f(t_i^m) \cong k_f^{(0)}(t_i^m) = k_f(t_i) \tag{75}$$

to calculate an approximate value of Y at t_{i+1}, denoted as $Y^{(0)}(t_{i+1})$, from eq. (72). An approximate value of k_f at t_{i+1}, denoted as $k_f^{(0)}(t_{i+1})$, is then calculated from the following equation:

$$\begin{aligned} k_f(t_{i+1}) &= k'_{eq} - (k'_{eq})^2 \int_0^{t_{i+1}} d\tau [1 - K_{eq}^{-1}\phi(\tau)]\Delta(t_{i+1}-\tau) \\ &\quad + (k'_{eq})^2 \int_0^{t_{i+1}} d\tau\ K_{eq}^{-1}\phi(\tau)\alpha(\tau)\Delta_f(t_{i+1}-\tau) \\ &\cong k'_{eq} - (k'_{eq})^2 \sum_{j=0}^{i} [1 - K_{eq}^{-1}\phi(t_j^m)] \int_{t_j}^{t_{j+1}} d\tau\ \Delta(t_{i+1}-\tau) \\ &\quad + (k'_{eq})^2 \sum_{j=0}^{i} K_{eq}^{-1}\phi(t_j^m)\alpha(t_j^m) \int_{t_j}^{t_{j-1}} d\tau\ \Delta_f(t_{i+1}-\tau) \end{aligned} \tag{76}$$

where $t_0 = 0$. We have assumed that $\phi(t)$ and $\alpha(t)$ vary much more smoothly with time than $\Delta(t)$ and $\Delta_f(t)$ so that when the time step size is small enough they may be assumed to vary linearly with time in each time step. The integrals involving the memory kernels may be evaluated analytically if the expressions given by eqs. (59) and (62) are assumed for $\Delta(t)$ and $\Delta_f(t)$, respectively:

$$\begin{aligned} \int_{t_j}^{t_{j+1}} d\tau\ \Delta(t_{i+1}-\tau) &= \int_{t_{i+1}-t_{j+1}}^{t_{i+1}-t_j} d\tau\ \Delta(\tau) \\ &= \Psi(t_{i+1}-t_j) - \Psi(t_{i+1}-t_{j+1}) \end{aligned} \tag{77}$$

$$\begin{aligned} \int_{t_j}^{t_{j+1}} d\tau\ \Delta_f(t_{i+1}-\tau) &= \int_{t_{i+1}-t_{j-1}}^{t_{i+1}-t_j} d\tau\ \Delta_f(\tau) \\ &= \Psi_f(t_{i+1}-t_j) - \Psi_f(t_{i-1}-t_{j+1}) \end{aligned} \tag{78}$$

where

$$\Psi(t) = (k'_{eq} + k_D)^{-1}[1 - \Omega(At^{1/2})] \tag{79}$$

$$\begin{aligned} \Psi_f(t) = \frac{(\sigma/\sigma_d)}{k'_{eq} + k_D} \exp(-B^2/4t)\Big[\Omega\Big(\frac{1}{2}Bt^{-1/2}\Big) \\ - \Omega\Big(\frac{1}{2}Bt^{-1/2} + At^{1/2}\Big)\Big] \end{aligned} \tag{80}$$

where $A = (1 + k'_{eq}/k_D)(D^{1/2}/\sigma)$ and $B = D^{-1/2}(\sigma_d - \sigma)$ as before, and the function $\Omega(y)$ was defined by eq. (60). Values of $\phi(t_j^m)$ and $\alpha(t_j^m)$ are assumed to be given by

$$\phi(t_j^m) = [\phi(t_j) + \phi(t_{j+1})]/2 \tag{81}$$

$$\alpha(t_j^m) = [\alpha(t_j) + \alpha(t_{j+1})]/2 \tag{82}$$

The values of $Y^{(0)}(t_{i+1})$ and $k_f^{(0)}(t_{i+1})$ are then used to give better approximations to $Y(t_i^m)$ and $k_f(t_i^m)$:

$$Y(t_i^m) \cong Y^{(1)}(t_i^m) = [Y(t_i) + Y^{(0)}(t_{i+1})]/2 \tag{83}$$

$$k_f(t_i^m) \cong k_f^{(1)}(t_i^m) = [k_f(t_i) + k_f^{(0)}(t_{i+1})]/2 \tag{84}$$

These values of $Y(t_i^m)$ and $k_f(t_i^m)$ may then be used to obtain better approximations to $Y(t_{i+1})$ and $k_f(t_{i+1})$, and so on. The iterative procedure is continued until the relative change in the value of $Y(t_{i+1})$ is less than 10^{-3} or so.

Pseudo first-order case. In Figure 1, we compare the numerical predictions of the present theory with that of the conventional theory as obtained by eq. (70). The values of input parameters σ, D and k'_{eq} are those estimated for the protoheme-CO system at 280 K[20]: $\sigma = 1.5$ Å, $D = 9.4 \times 10^{-8}$ cm²/s, $k'_{eq} = 5.0 \times 10^{-14}$ cm³/s, $C_B = 4.5 \times 10^{-4}$ M, and $C_0 = 5.0 \times 10^{-5}$ M. The value of k_D is taken to be $2\pi\sigma D$ rather than $4\pi\sigma D$ for the reason described by Szabo *et al.*[20]. The irradiation function defined by eq. (44) is assumed to be given by

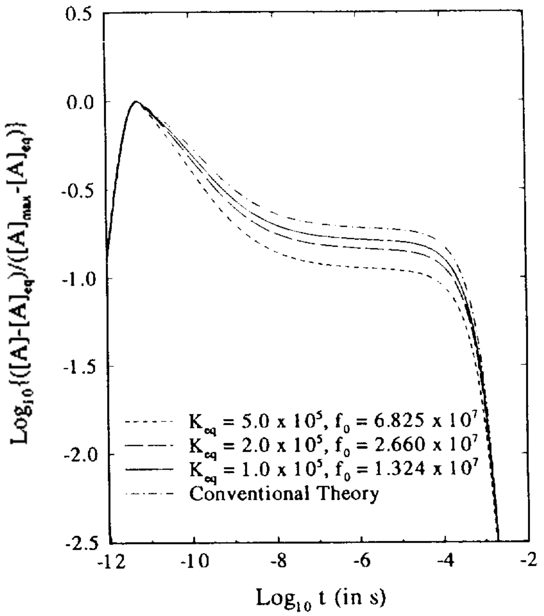

Figure 1. K_{eq} dependence of the variation of $[A]$ with time in the pseudo first-order case. Values of model parameters used in the calculation are described in the text.

$$\alpha(t) = f_o(t/t_L)\ \exp\Big\{-\frac{1}{2}[(t/t_L)^2 - 1]\Big\} \tag{85}$$

The value of t_L representing the width of the photolytic pulse is set equal to 2 ps. The magnitude of the radiation intensity parameter f_o is adjusted such that the fraction of photolyzed molecules has the peak value of 0.0100 (*i.e.*, $([A]_{max} - [A]_{eq})/C_0 = 0.0100$ where $[A]_{max}$ and $[A]_{eq}$ denote the peak concentration and equilibrium concentration of A molecules, respectively). In the present theory values of additional parameters σ_d and $K_{eq}(= k'_{eq}/k'_r)$ are needed. We assume that $\sigma_d = \sigma$ and the value of K_{eq} is adjusted to fit the experimental data[20]. In Figure 1, the solid curve obtained with $K_{eq} = 1.0 \times 10^5$ M^{-1} gives the best fit to the experimental data. It should be noted that the value of f_o has been adjusted but that it is not a free parameter since it must have a fixed value to give the known fraction of photolyzed molecules. Since experimental data on the actual fraction of photolyzed molecules are not available to us, we have simply assumed that $([A]_{max} - [A]_{eq})/C_0 = 0.0100$ in obtaining Figure 1. As K_{eq} is increased with k'_{eq} fixed, the photodissociation rate constant $k_p(t)$ $[= k'_{eq}\alpha(t)]$ decreases for a given value of f_o. Hence in order to give the same fraction of photolyzed molecules, the value of f_o needs to be increased as K_{eq} increases. It is amusing that the adjusted value of K_{eq} is in agreement with the known experimental value[21], $K_{eq} = 5 \times 10^4$ M^{-1}. Figure 1 shows that K_{eq} should be the key parameter required in the analysis

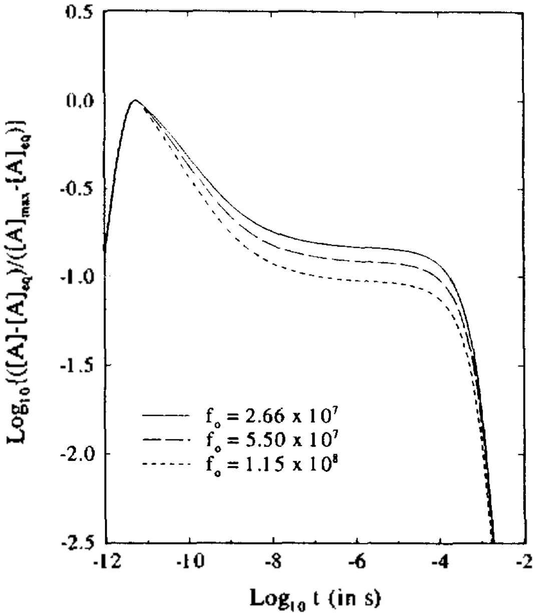

Figure 2. Dependence of the scaled decay curves on the intensity of photolytic radiation in the pseudo first-order case. Values of model parameters used in the calculation are described in the text.

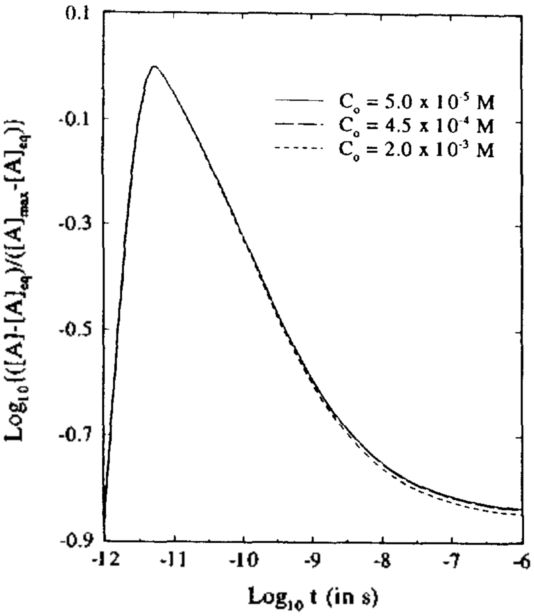

Figure 3. Dependence of the scaled decay curves on the initial concentration of parent molecules in the pseudo first-order case. Values of model parameters used in the calculation are described in the text.

of the time-resolved kinetic data of photolytic experiments. Nevertheless, no previous theories have dealt with this aspect properly. Finally, the deviation of the dot-dashed curve in Figure 1, which is calculated by the conventional theory [eq. (70)], from the experimental data shows that the convoultion integral expression may not properly describe the data obtained using a photolytic pulse with finite width. The values of parameters σ, D and k'_{eq} were obtained in ref.[20] from the fitting of long-time data to the expression of the survival probability,

$$S_{conv}(t) \cong S^{SZ}(t) = F^{SZ}_{gem}(t)\ F_{bimol}(t) \tag{86}$$

where

$$F^{SZ}_{gem}(t) = \left(\frac{k_D}{k'_{eq}+k_D}\right)\left[1+\left(\frac{k'_{eq}}{k_D}\right)\ \Omega(At^{1/2})\right] \tag{87}$$

$$F_{bimol}(t) = \exp\left\{-C_B\left(\frac{k'_{eq}\ k_D}{k'_{eq}+k_D}\right)\left[t+\frac{k'_{eq}\ k_D}{(k'_{eq}+k_D)^2}\ \frac{\sigma^2}{D} \times\left(2(A^2t/\pi)^{1/2}-1+\Omega(At^{1/2})\right)\right]\right\} \tag{88}$$

Figure 2 shows the effect of photolytic radiation intensity, gauged by the parameter f_o, with the value of K_{eq} fixed at 2.0×10^5 M^{-1}. Values of parameters other than f_o and K_{eq} are the same as in Figure 1. As the radiation intensity increases, the curve decays more rapidly. Nevertheless, no previous theories have dealt with this aspect properly.

Figure 3 shows that the concentration effect on the decay curves may not be appreciable in the pseudo first-order case where $C_B \gg C_0$, although the curve appears to decay a little faster for a larger value of C_0. Except that $K_{eq}=2.0\times10^5$ M^{-1}, $f_o=2.66\times10^7$, and the value of C_0 is varied, values of other parameters used in the calculation are the same as in Figure 1.

Figure 4 displays the variation of the decay curves for different values of σ_d. Except that $K_{eq}=2.0\times10^5$ M^{-1}, $f_o=2.66\times10^7$, and the value of σ_d is varied, values of other parameters used in the calculation are the same as in Figure 1. As expected, a larger value of σ_d gives the slower decay of A molecule concentration.

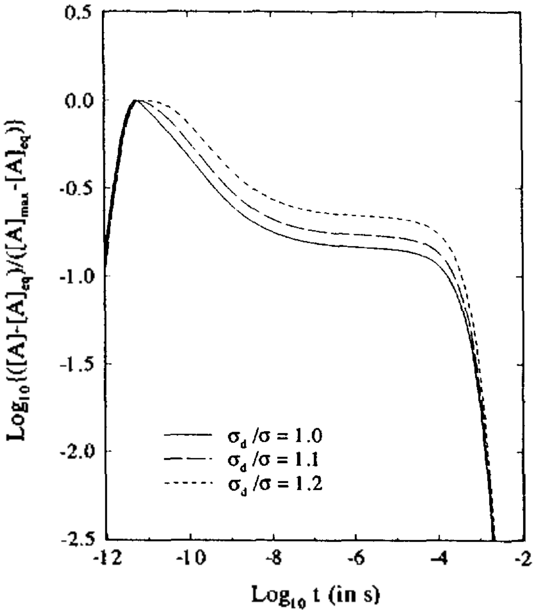

Figure 4. Dependence of the scaled decay curves on the ratio σ_d/σ in the pseudo first-order case. Values of model parameters used in the calculation are described in the text.

Second-order case. Figure 5 displays the decay curves of A molecule concentration in the second-order case with $C_B=0$. The values of input parameters σ, D, and k'_{eq} are those estimated for the iodine atom recombination[9,22-26]; $\sigma=4.32$

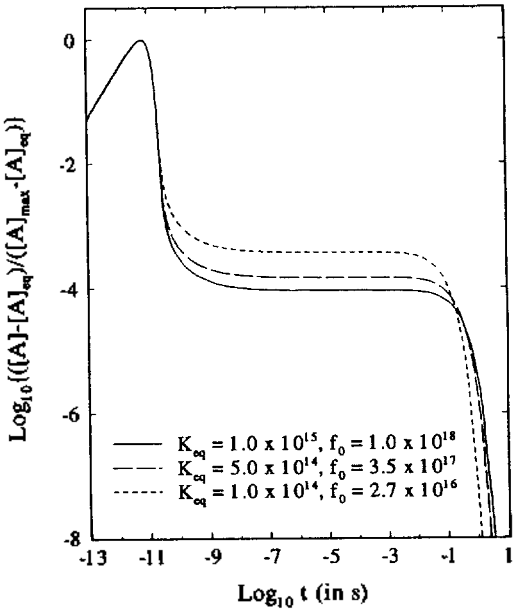

Figure 5. K_{eq} dependence of the variation of $[A]$ with time in the second-order case. Values of model parameters used in the calculation are described in the text.

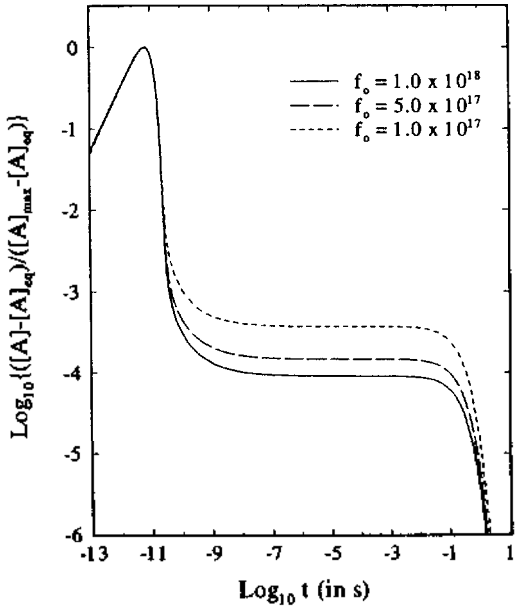

Figure 6. Dependence of the scaled decay curves on the intensity of photolytic radiation in the second-order case. Values of model parameters used in the calculation are described in the text.

Å, $D=2.0\times10^{-5}$ cm²/s, and $k_{eq}^{f}=2.0\times10^{-11}$ cm³/s. We assume that $\sigma_d=\sigma$, and the value of K_{eq} has been varied as shown. The irradiation function $\alpha(t)$ is assumed to be given by Eq. (85) with $t_L=5$ ps. The radiation intensity parameter f_0 is adjusted such that the fraction of photolyzed molecules has the peak value of 0.030 (*i.e.*, $([A]_{max}-[A]_{eq})/C_0=0.030$). The initial concentration C_0 of C molecules before the onset of photodissociation is set equal to 1.0×10^{-4} M. As in the pseudo first-order case, the concentration of A decays faster as the equilibrium constant K_{eq} increases.

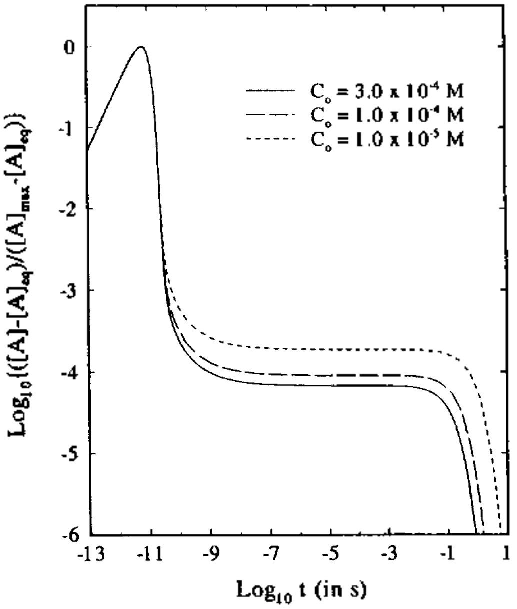

Figure 7. Dependence of the scaled decay curves on the initial concentration of parent molecules in the second-order case. Values of model parameters used in the calculation are described in the text.

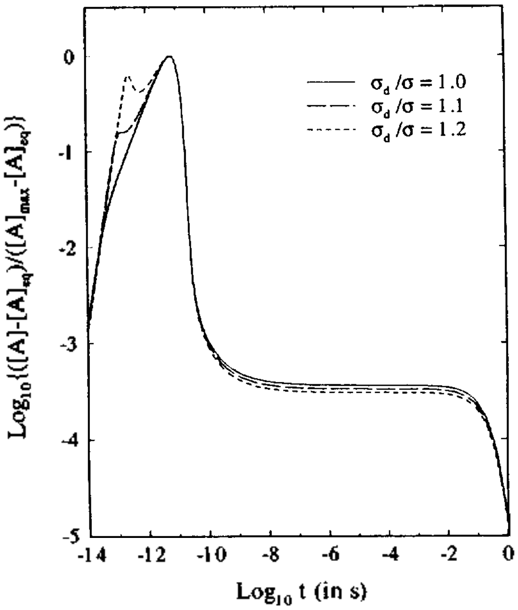

Figure 8. Dependence of the scaled decay curves on the ratio σ_d/σ in the second-order case. Values of model parameters used in the calculation are described in the text.

Figure 6 shows the effect of photolytic radiation intensity on the shape of the decay curve. Except that $K_{eq}=1.0\times10^{15}$ M^{-1} and the value of f_0 is varied as shown in the figure, values of other parameters used in the calculation are the same as in Figure 5. As the radiation intensity increases, the curve decays more rapidly.

Figure 7 shows that the concentration effect on the decay curves should be large in the second-order case. As the initial concentration C_0 gets larger, the curve decays faster. Except that $K_{eq}=1.0\times10^{15}$ M^{-1}, $f_o=1.0\times10^{17}$, and the value of C_0 is varied, values of other parameters used in the calculation are the same as in Figure 5.

Figure 8 displays the variation of the decay curves for different values of σ_d. Except that $K_{eq}=1.0\times10^{15}$ M^{-1}, $f_o=1.0\times10^{17}$, and the value of σ_d is varied, values of other parameters used in the calculation are the same as in Figure 5. It is interesting that the scaled curve decays a little faster at intermediate times when the photolytic separation σ_d is larger than the thermolytic separation σ than when $\sigma_d=\sigma$. Another interesting observation is that the curve has a hump in the subpicosecond time region when $\sigma_d>\sigma$. Although severe experimental difficulties are expected to probe such a short time region, observation of the hump will provide a definite evidence that $\sigma_d>\sigma$.

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