

KINETICS OF PARTLY DIFFUSION-CONTROLLED REACTIONS V: ANALYSES OF QUENCHING INVOLVING ENERGY TRANSFER FROM TWO STATES

J. C. ANDRÉ and M. BOUCHY

*Laboratoire de Chimie Générale, E.R.A. n° 136 du C.N.R.S., 1 rue Grandville,
54042 Nancy Cédex (France)*

W. R. WARE

*The Photochemistry Unit, Department of Chemistry, University of Western Ontario,
London, Ontario N6A 5B7 (Canada)*

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Summary

In this paper we present general equations for the treatment of sensitized reactions when two different excited states of the sensitizer both contribute to the photosensitization. In the case of diffusion-controlled reactions, classical equations based on stationary diffusion are not valid under the usual experimental conditions and have to be modified. We propose a kinetic model which takes into account static quenching and non-stationary diffusion.

1. Introduction

In a recent paper Wagner [1] has pointed out the interest in kinetic studies of inhibition for the determination of the lifetime of excited states and of the quantum yields of intersystem crossing. In particular, it is shown that the sensitization yield of electronic energy transfer gives valuable information including the detection of more than one donor excited state and the lifetimes of these states. An extensive set of relationships is given to aid the interpretation of experimental data.

However, in the particular case of very short lifetimes, ranging from 10 ps to 1 ns, the kinetics of sensitization are in fact that of a practically diffusion-controlled reaction, and lead for conventional solvents to the use of quencher concentrations between 10 and 0.1 mol l⁻¹. If the reaction is not diffusion controlled the concentrations have to be much larger than this, a situation which cannot be realized in practice. Under these conditions the only answer is to look for diffusion-controlled transfer reactions. We have shown [2 - 4], in agreement with earlier studies (see for example refs. 5 and 6), that for very short lifetimes, usually shorter than 100 ns, and in conventional solvents non-stationary processes must intervene; this does not allow us to use simplified relationships which require the apparent rate constants

to be time independent. Moreover, for the quencher concentrations concerned, static quenching can occur and can perturb the kinetics.

We intend in this work to show the influence of the phenomena of non-stationary diffusion and static quenching on partly diffusion-controlled reactions of sensitization and to give a more extensive theoretical treatment in terms of a competition between "chemical" and "diffusional" kinetics.

2. Review of partly diffusion-controlled reactions

2.1. Review of the principles of the treatment of diffusion-controlled reactions

The conventional treatment first used by von Smoluchovski [7] is as follows, where A and B are the reactive species (see Fig. 1).

(1) A particular A molecule is used as a relative reference of the motion of surrounding B molecules in a system of spherical symmetry (*i.e.* the only space coordinate is the distance r measured from A).

(2) To solve the description of the relative motion of these B molecules, we "superpose" a large number of particular systems as in (1) and define an average A molecule surrounded by a continuous distribution of B molecules

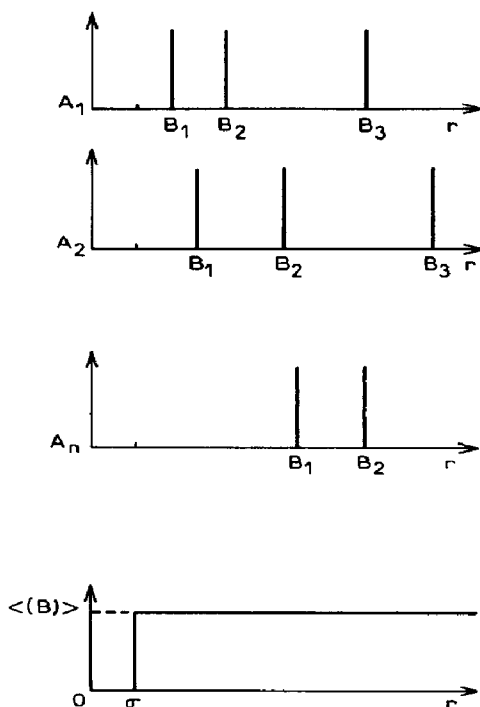


Fig. 1. Use of the superposition rule to obtain a mean continuous distribution of B molecules around A molecules. A_1, A_2, \dots, A_n are particular A molecules surrounded by B_1, B_2, \dots . The lower curve is obtained by superposition of the representations above (σ is the encounter distance).

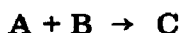
(i.e. a local concentration $[B(r, t)]$) to which Fick's laws of diffusion can be applied.

Let us note the following further assumptions. (a) The concentration of A molecules is sufficiently low so that they can be considered to be independent. (b) The relative diffusion coefficient of B towards A is taken as the sum of the diffusion coefficients of A and B, independent of concentration. (c) There is no mutual electrical potential between A and B.

2.2. Mathematical treatment

2.2.1. Strictly diffusion-controlled reactions

Let us consider a homogeneous population of spherical molecules B in solution in an inert solvent and the generation at a time $t = 0$ of spherical reacting molecules A (produced by light excitation, for example). The molecules A react with the molecules B:



Let us then consider that every encounter leads to chemical reaction, i.e. that the reaction can occur during an infinitesimal time. Then we can determine the apparent rate constant $k_a(t)$ of the reaction using the following relation, given previously by Wilemski and Fixman [8]:

$$\partial\phi(r,t)/\partial t + \mathcal{G}\phi(r,t) = 0 \quad (1)$$

Here ϕ is a distribution function and is the ratio of the local concentration of B to the mean concentration $\langle[B]\rangle$ of B, i.e. $\phi(r,t) = [B(r,t)]/\langle[B]\rangle$; r is the distance between the centres of a molecule A and a molecule B; \mathcal{G} is the time evolution operator (relating to the diffusion process). For uncharged particles we can write

$$\mathcal{G} \equiv -D\nabla^2$$

where D is the sum of the diffusion constants of the two species A and B and ∇^2 is the laplacian operator.

The resolution of this system leads to the classical expression of the apparent rate constant $k_a(t)$ [2], i.e. to

$$k_a(t) = 4\pi N\sigma D \{1 + \sigma(\pi Dt)^{-1/2}\} \quad (2)$$

where σ is the encounter distance (between the centres of the encountering molecules) and N is Avogadro's number.

At times much longer than σ^2/D , $k_a(t)$ is approximately equal to $4\pi N\sigma D$ and stationary state diffusion takes place; the instantaneous rate constant then is almost time independent.

In contrast, at times shorter than σ^2/D , or near to this value, $k_a(t)$ is time dependent; this leads to non-stationary state diffusion kinetics.

2.2.2. Reactions dependent in part on diffusion

If the chemical reaction between A and B does not occur with an infinite rate constant, as supposed in Section 2.2.1, but occurs with a rate

constant $k(r)^*$ which is dependent on the distance r between A and B, the former treatment is no longer applicable and a new treatment is required.

2.2.2.1. Equations which define the reacting system. Using the formulation of Wilemski and Fixman [8] and of Doi [9], relation (1) can be written as

$$\partial\phi(r, t)/\partial t + \mathcal{G}\phi(r, t) = -k(r)\phi(r, t) \quad (3)$$

Knowing \mathcal{G} and $k(r)$ it is possible to determine the variation of $\phi(r, t)$ with t , either using Green's functions [8] or using the Laplace transform or numerical techniques. The apparent rate constant is given by the expression

$$k_a(t) = \int_{\sigma}^{\infty} 4\pi r^2 N k(r) \phi(r, t) dr \quad (4)$$

2.2.2.2. Expression of $k(r)$. In the case where a chemical reaction occurs as discussed, the variations of $k(r)$ are not well known and a simplified model must be used. Reaction or interaction between molecules requires the overlap of the external molecular orbitals of the two molecules. The value of the overlap of molecular orbitals is known (see for example ref. 10); it is a decreasing function of r and beyond a value of r of some ångströms there is practically no overlap. In this sense the problem is very similar to the case of electronic energy transfer described by Dexter [11].

In the case of resonance energy transfer described by Förster [12], the expression of $k(r)$ is well known and rigorous computing could be possible. However, here we consider only interactions at short distances.

In our model we suppose that $k(r)$ is approximately constant and equal to a given value k for a distance smaller than a given value σ' (i.e. for $\sigma < r < \sigma'$) and that $k(r)$ is negligible for r greater than σ' . Then expression (4) becomes

$$k_a(t) = \int_{\sigma}^{\sigma'} 4\pi r^2 N k \phi(r, t) dr \quad (5)$$

2.2.2.3. Expression of \mathcal{G} . The operator \mathcal{G} is determined using classical macroscopic concepts well known in the case of diffusion in the solid state and also applicable here. The expression of the flow J of particles is given by

$$J = -D\nabla[B] \quad (6)$$

$\phi(r, t)$ is derived from eqn. (4) together with Fick's second law, i.e.

$$\partial\phi/\partial t = -\nabla J/[B] \quad (7)$$

By assuming $\nabla D = 0$, $\mathcal{G}\phi$ is given by

*For two particles A and B at a distance r , the probability of chemical reaction during time dt is equal to $k(r) dt$.

$$\mathcal{G}\phi = -D\nabla^2\phi \quad (8)$$

Thus a diffusion model is developed by considering two distinct volumes in the reacting system centred on a molecule A towards which molecules B diffuse (see Fig. 2):

(1) a reaction range comprised of the volume between a sphere of radius σ' and a sphere of radius σ wherein the chemical reaction occurs with a rate constant k ; we assume that no diffusion occurs in this range, i.e. $\phi(r, t)$ is independent of r ;

(2) an external volume ($r > \sigma'$) in which no chemical reaction but only diffusion occurs.

2.2.2.4. Equations which define the system in our simplified model (see Fig. 2). For $r \geq \sigma'$

$$\frac{\partial\phi}{\partial t} = D\nabla^2\phi = D\left(\frac{\partial^2\phi}{\partial r^2} + \frac{2}{r}\frac{\partial\phi}{\partial r}\right) \quad (9)$$

For $\sigma \leq r < \sigma'$, the flow of molecules B at a distance σ' from A has to be equal to both the accumulation of B inside the reaction volume and the disappearance of B in the chemical reaction $A + B \rightarrow C$. Thus, we must have

$$4\pi N\sigma'^2 D\left(\frac{\partial\phi}{\partial r}\right)_{\sigma'} \langle [B] \rangle = \frac{4}{3}\pi N(\sigma'^3 - \sigma^3) \frac{d\phi^\circ}{dt} \langle [B] \rangle + \frac{4}{3}\pi N(\sigma'^3 - \sigma^3) k\phi^\circ \langle [B] \rangle \quad (10)$$

where ϕ° represents the value of ϕ inside the reaction range.

The macroscopic bimolecular rate constant k_c ($\text{mol}^{-1} \text{s}^{-1}$) is related to the rate constant k by the equation

$$\frac{\partial[C]}{\partial t} = k_c[A][B^\circ] = [A]N[B^\circ] \int_{\sigma}^{\sigma'} 4\pi r^2 k dr$$

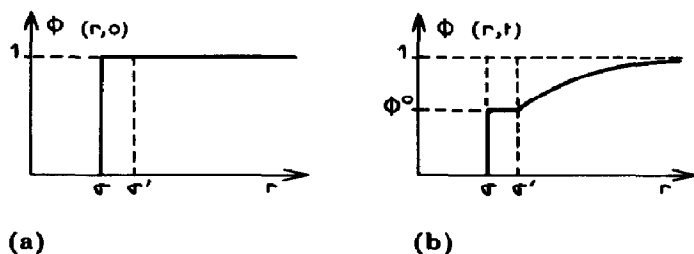


Fig. 2. Separation of space into two volumes where chemical reaction ($r < \sigma'$) and diffusion ($r > \sigma'$) occur: (a) distribution at time $t = 0$; (b) distribution at time $t > 0$.

where $[B^\circ]$ represents the value of $[B(r, t)]$ inside the reaction range. Then

$$k_c = \frac{4}{3}\pi N(\sigma'^3 - \sigma^3)k = NV_1 k = 4\pi N\sigma'^3 \alpha k \quad (11)$$

with

$$\alpha = \frac{1}{3} \left\{ 1 - \left(\frac{\sigma}{\sigma'} \right)^3 \right\}$$

By including this macroscopic term in relation (10), we obtain the following relation:

$$k_0 \sigma' (\partial \phi / \partial r)_{\sigma'} = NV_1 (d\phi / dt)_{\sigma'} + k_c (\phi)_{\sigma'} \quad (12)$$

where $k_0 = 4\pi N\sigma'D$.

Equations (9) and (12) together define the system.

2.2.2.5. Apparent rate constant k_a . Assuming $\tau = Dt/\sigma'^2$, we obtain from eqn. (5)

$$k_a(\tau) = NV_1 k \phi^\circ(\tau) = k_c \phi^\circ(\tau) \quad (13)$$

The variations of $k_a(\tau)$ are therefore given by the expression of $\phi^\circ(\tau)$.

2.2.2.6. Simplified relationships. At large values of time we obtain

$$\phi^\circ(\tau) \approx \frac{1}{\beta + 1} \left\{ 1 + \frac{\beta}{\beta + 1} (\pi\tau)^{-1/2} \right\} \quad (14)$$

with

$$\beta = k_c/k_0$$

and

$$k_a(t) \approx \frac{k_0 k_c}{k_0 + k_c} \left\{ 1 + \frac{k_c}{k_c + k_0} \frac{\sigma'}{(\pi Dt)^{1/2}} \right\} \quad (15)$$

This simplified relationship is identical with that proposed by Nemzek and Ware [5].

When t increases infinitely we obtain

$$\lim_{t \rightarrow \infty} k_a = \frac{k_c}{1 + k_c/k_0} \quad \text{or} \quad \lim_{t \rightarrow \infty} \frac{1}{k_a} = \frac{1}{k_c} + \frac{1}{k_0} \quad (16)$$

and when k_c/k_0 goes to infinity $k_a(t)$ becomes

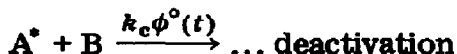
$$k_a(t) = k_0 \{ 1 + \sigma'(\pi Dt)^{-1/2} \}$$

which is identical with relationship (2) given in Section 2.2.1, except for the value of σ which is now σ' .

Expression (15) can be used for experiments on fluorescence quenching using conventional flash excitation.

2.2.3. Consequences

Consider the following scheme for the deactivation of A^* :



Then after δ -pulse excitation

$$d[A^*]/dt = -\{k + k_c \langle [B] \rangle \phi^\circ(t)\} [A^*] \quad (17)$$

Equation (17) leads to

$$\frac{1}{[A^*]} \frac{d[A^*]}{d\tau} = -\left\{ \frac{k\sigma'^2}{D} + \frac{k_c \sigma'^2}{D} \langle [B] \rangle \phi^\circ(\tau) \right\} \quad (18)$$

with $\tau = Dt/\sigma'^2$. Then if

$$Z(t) \equiv \log([A^*]/[A^*]_{t=0})$$

for small values of τ (greater than or equal to 0.2), a good approximation of the time evolution of $Z(t)$ is

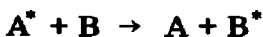
$$\begin{aligned} Z(t) &\approx -\left(k + \frac{k_c k_0}{k_c + k_0} \langle [B] \rangle\right) t - \frac{k_c^2 k_0}{(k_c + k_0)^2} \langle [B] \rangle \frac{2\sigma' t}{(\pi Dt)^{1/2}} - NV'_1 \langle [B] \rangle \\ &= -at - bt^{1/2} - c \end{aligned} \quad (19)$$

with

$$NV'_1 = 4\pi N\sigma'^3 \frac{k_c^2 k_0}{(k_c + k_0)^3} \left\{ \alpha \left(1 + \frac{k_c}{k_0}\right) - 1 \right\}$$

2.3. Photosensitization reaction

Taking into account the simplifying assumptions given in Sections 2.1 and 2.2, we can express the probability of photosensitization as



2.3.1. Probability of photosensitization at time $t = 0$

This is derived from relationship (19) as

$$p_s = 1 - \exp(-NV'_1 \langle [B] \rangle) \quad (20)$$

2.3.2. Probability of photosensitization at time $t > 0$

Knowing the concentration of A^* as a function of time we can calculate the rate of energy transfer

$$r = k_s(t) \langle [B] \rangle [A^*]$$

leading to a probability of sensitization over the lifetime of A^* of

$$p_d = \exp(-NV_1'\langle[B]\rangle) \left\{ 1 - I(\lambda') \left(1 + \frac{k_0 k_c}{k_0 + k_c} \tau_0 \langle[B]\rangle \right)^{-1} \right\} \quad (21)$$

where τ_0 is the natural lifetime of A^* and

$$I(\lambda') = \int_0^\infty \exp(-au - \lambda'u^{1/2}) du$$

with

$$a = \frac{1}{\tau_0} + \frac{k_c k_0}{k_0 + k_c} \langle[B]\rangle$$

and

$$\lambda' = \frac{2\sigma'}{(\pi D\tau)^{1/2}} \frac{k_c^2 k_0 \tau_0 \langle[B]\rangle}{(k_c + k_0)^2} \left(1 + \frac{k_c k_0}{k_c + k_0} \tau_0 \langle[B]\rangle \right)^{-1/2}$$

Then the overall probability of photosensitization can be written as

$$p = p_s + p_d \approx 1 - I(\lambda') \exp(-NV_1'\langle[B]\rangle) \left(1 + \frac{k_c k_0}{k_c + k_0} \tau_0 \langle[B]\rangle \right)^{-1} \quad (22)$$

2.3.3. Linear representation

For long lifetimes of A^* (in practice larger than 100 ns) and in usual (low viscosity) solvents it can be shown that

$$\lambda' \approx 0 \quad I(\lambda') \approx 1 \quad NV_1'\langle[B]\rangle \approx 0$$

Then

$$\frac{1}{p} \approx 1 + \left(\frac{k_0 + k_c}{k_0 k_c} \frac{1}{\tau_0} \right) \frac{1}{\langle[B]\rangle} \quad (23)$$

This relationship is close to that used by Wagner and coworkers [1, 13, 14].

Figures 3(a) and 3(b) show the effect of static quenching and non-stationary quenching on a plot of $1/p$ against $1/\langle[B]\rangle$ in a practical example. In particular they indicate that these phenomena lead to a much higher value of p and to a non-linear relationship between $1/p$ and $1/\langle[B]\rangle$. Moreover, if an approximate linear variation is plotted from experimental data, wrongly assuming the validity of relationship (23), incorrect values of the parameters are obtained, as pointed out in ref. 4.

Besides, under these conditions it becomes very difficult to carry out a kinetic treatment capable of handling experimental data when two donors are involved since other problems arise. These are discussed in Section 3.

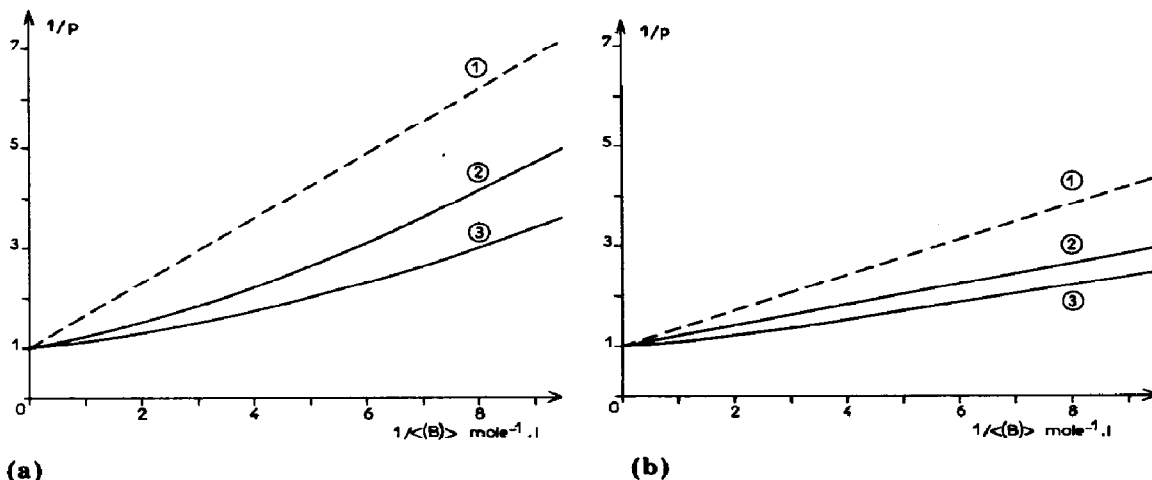
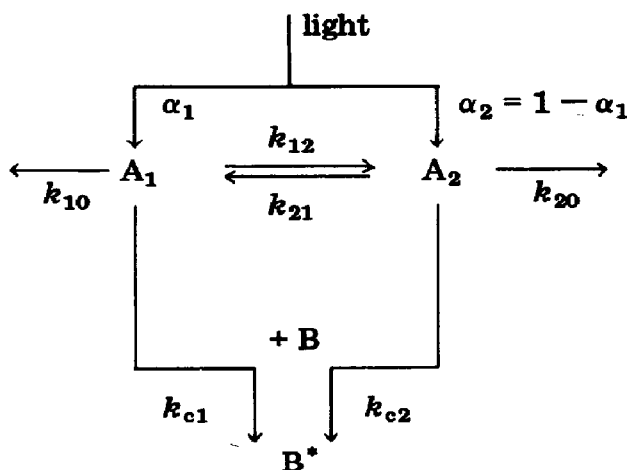


Fig. 3. Representations of $1/p$ vs. $1/[B]$: (a) a strictly diffusion-controlled reaction, $k_c > k_0$, $\sigma = 6 \text{ \AA}$, $D = 1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; (b) a partly diffusion-controlled reaction, $k_c/k_0 = 3$, $\sigma = 6 \text{ \AA}$, $D = 0.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\sigma' = 10 \text{ \AA}$. In both cases curve 1 is drawn from relation (23) by neglecting static quenching and non-stationary diffusion, curve 2 is drawn from relation (22) assuming no static quenching ($\sigma = \sigma' = 6 \text{ \AA}$) and curve 3 is drawn from relation (22) taking into account both static quenching and non-stationary diffusion.

3. Photosensitization where two electronically excited donor states contribute

Let us consider the following scheme [1]:



where α_1 and α_2 are the probabilities of formation of A_1 and A_2 respectively. We shall assume in the following that the reacting distance σ' is the same in both sensitization processes.

The kinetic treatment can be carried out to give the values of the rate constants. However, relationship (15) giving the rate constant of sensitization is not valid in this case. It is derived by expressing the diffusion of B molecules around an average A molecule starting from a random distribution at time $t = 0$ of the appearance of A. In the case of two interacting donors A_1 and A_2 , when such an excited molecule is formed by irradiation, relationship (15) is in general still valid. However, when A_1 for example originates from the other type A_2 by intersystem crossing, the distribution of B molecules is no longer random at time $t = 0$ because it is that which was around the A_2 molecule at the time when it was generated from an A_1 molecule. This interconnection between the distribution functions of B, ϕ_1 around A_1 and ϕ_2 around A_2 , is schematically represented in Fig. 4; the evolution during differential time dt is decomposed in two parts, the diffusion of B around A_1 and A_2 and then the exchange between A_1 and A_2 by intersystem crossing which alters the distribution functions ϕ_1 and ϕ_2 .

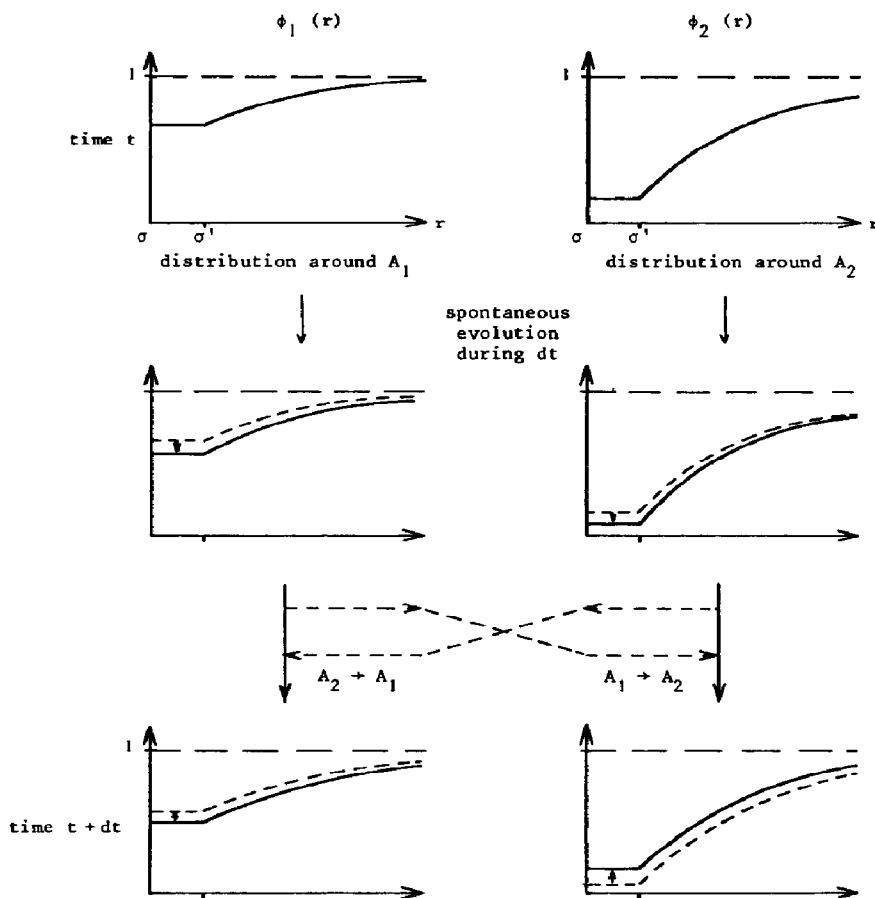


Fig. 4. Representations of the influence of exchange between A_1 and A_2 on the distribution functions ϕ_1 and ϕ_2 .

3.1. Equations defining the reacting system

3.1.1. Time evolution terms of ϕ_1 and ϕ_2 for $r \geq \sigma'$

Let $[B_1(r, t)]$ and $[B_2(r, t)]$ be the mean local concentrations of B around A_1 and A_2 respectively and let us consider that, at time $t = 0$, N_1° and N_2° molecules of the types A_1 and A_2 respectively are formed.

At time t these numbers become $N_1(t)$ and $N_2(t)$ and their values at time $t + dt$ can then be derived as follows:

$$N_1(t + dt) = N_1(t) - \frac{dt}{\tau_1} N_1(t) + k_{21} dt N_2(t + dt)$$

$$N_2(t + dt) = N_2(t) - \frac{dt}{\tau_2} N_2(t) + k_{12} dt N_1(t + dt)$$

where

$$1/\tau_1 = k_{10} + k_{12} + k_{c1} \langle [B] \rangle \phi_1^\circ(t)$$

$$1/\tau_2 = k_{20} + k_{21} + k_{c2} \langle [B] \rangle \phi_2^\circ(t)$$

ϕ_1° and ϕ_2° are the values of the configurational distribution functions ϕ_1 and ϕ_2 at distance σ' . The time evolutions of the concentrations $[B_1(r, t)]$ and $[B_2(r, t)]$ are then expressed as, for example for B_1 ,

$$[B_1(r, t + dt)] N_1(t + dt) = \{ [B_1(r, t)] - \mathcal{G}[B_1(r, t)] dt \} N_1(t) (1 - dt/\tau_1) + [B_2(r, t + dt)] k_{21} dt N_2(t + dt)$$

which become

$$\frac{\partial [B_1]}{\partial t} + \mathcal{G}[B_1] = k_{21} \frac{N_2}{N_1} ([B_2] - [B_1])$$

$$\frac{\partial [B_2]}{\partial t} + \mathcal{G}[B_2] = k_{12} \frac{N_1}{N_2} ([B_1] - [B_2])$$

This can be expressed in terms of the configurational distribution functions ϕ_1 and ϕ_2 and of the concentrations $[A_1]$ and $[A_2]$ of the donors:

$$\frac{\partial \phi_1}{\partial t} + \mathcal{G}\phi_1 = k_{21} \frac{[A_2]}{[A_1]} (\phi_2 - \phi_1) \tag{24}$$

$$\frac{\partial \phi_2}{\partial t} + \mathcal{G}\phi_2 = k_{12} \frac{[A_1]}{[A_2]} (\phi_1 - \phi_2)$$

Introduction of $\mathcal{G} = -D\nabla^2$ as the time evolution operator gives

$$\frac{\partial \phi_1}{\partial t} = D_1 \nabla^2 \phi_1 + k_{21} \frac{[A_2]}{[A_1]} (\phi_2 - \phi_1) \tag{25}$$

$$\frac{\partial \phi_2}{\partial t} = D_2 \nabla^2 \phi_2 + k_{12} \frac{[A_1]}{[A_2]} (\phi_1 - \phi_2)$$

where D_1 and D_2 are the relative diffusion coefficients of B towards A_1 and A_2 respectively. The reasonable assumption that D_1 and D_2 are equal can be made, since A_1 and A_2 are the same molecule:

$$D_1 \approx D_2 \approx D$$

3.1.2. Time evolution terms of ϕ_1 and ϕ_2 for $\sigma \leq r < \sigma'$

In the absence of intersystem crossing between A_1 and A_2 , we would write for example for A_1

$$4\pi N\sigma'^2 D \left(\frac{\partial [B_1]}{\partial r} \right)_{\sigma'} = NV_1 \frac{\partial [B_1^\circ]}{\partial t} + NV_1 k_{c1} [B_1^\circ]$$

where $[B_1^\circ]$ and $[B_2^\circ]$ are the values of $[B_1(r, t)]$ and $[B_2(r, t)]$ respectively for $\sigma \leq r \leq \sigma'$.

When there is an exchange between A_1 and A_2 , following the same principle as in Section 3.1.1, this becomes

$$\begin{aligned} NV_1 [B_1^\circ(t + dt)] N_1(t + dt) = & \{ NV_1 [B_1^\circ(t)] + 4\pi N\sigma'^2 D (\partial [B_1] / \partial r)_{\sigma'} - \\ & - k_{c2} NV_1 [B_1^\circ(t)] \} N_1(t) (1 - dt/\tau_1) + \\ & + NV_1 [B_2^\circ(t + dt)] k_{21} dt N_2(t + dt) \end{aligned}$$

which leads to

$$\begin{aligned} NV_1 \frac{d[B_1^\circ]}{dt} = & 4\pi N\sigma'^2 D \left(\frac{\partial [B_1]}{\partial r} \right)_{\sigma'} - k_{c1} NV_1 [B_1^\circ(t)] + \\ & + NV_1 k_{21} \frac{[A_2]}{[A_1]} \{ [B_2^\circ(t + dt)] - [B_1^\circ(t + dt)] \} \end{aligned}$$

and

$$\begin{aligned} \frac{d\phi_1^\circ}{dt} = & \frac{4\pi N\sigma'^2 D (\partial \phi_1)}{NV_1 (\partial r)_{\sigma'}} - k_{c1} \phi_1^\circ + k_{21} \frac{[A_2]}{[A_1]} (\phi_2^\circ - \phi_1^\circ) \\ \frac{d\phi_2^\circ}{dt} = & \frac{4\pi N\sigma'^2 D (\partial \phi_2)}{NV_1 (\partial r)_{\sigma'}} - k_{c2} \phi_2^\circ + k_{12} \frac{[A_1]}{[A_2]} (\phi_1^\circ - \phi_2^\circ) \end{aligned} \quad (26)$$

3.1.3. Time evolution of $[A_1]$ and $[A_2]$

The rates of change of $[A_1]$ and $[A_2]$ with time are given by

$$\begin{aligned} \frac{d[A_1]}{dt} = & - (k_{10} + k_{12} + k_{c1} \langle [B] \rangle \phi_1^\circ) [A_1] + k_{21} [A_2] \\ \frac{d[A_2]}{dt} = & - (k_{20} + k_{21} + k_{c2} \langle [B] \rangle \phi_2^\circ) [A_2] + k_{12} [A_1] \end{aligned} \quad (27)$$

The set of six relationships (25), (26) and (27) defines the evolution of the reacting system.

3.1.4. Problems arising in the solution of the system

As the mathematical system defined is non-linear, it is not possible to find an analytical solution in Laplace or Fourier spaces. The only possibility is to carry out a numerical resolution leading to the values of $[A_1]$ and $[A_2]$ and therefore to the yield of energy transfer from A_1 and A_2 to B. One example is shown in Figs. 5 and 6 where ϕ_1 and ϕ_2 are represented to illustrate the effect of the exchange between A_1 and A_2 .

3.1.5. Remark on "superquenching"

An interesting example is the case where A_2 for instance is not liable to be quenched by B ($k_{c2} = 0$) whereas A_1 can be quenched. Under these conditions $\phi_2(r, t)$ is always higher than $\phi_1(r, t)$ and its contribution to the value of $\phi_1(r, t)$ leads to a value of ϕ_1° much greater than that which would be expected in the absence of exchange between A_1 and A_2 . This constant "feeding" of ϕ_1 leads to a deactivation which is more effective than when $k_{12} = k_{21} = 0$. This effect of "superquenching" is pictured in Figs. 5 and 6.

3.2. Study of the particular case where $k_{c1} = k_{c2}$

3.2.1. Expression of ϕ_1° and ϕ_2°

The system defined in Section 3.1 cannot be solved in the general case but a resolution can be carried out when $k_{c1} = k_{c2}$. Under these conditions we have indeed $\phi_1 = \phi_2 = \phi$ and $\phi_1^{\circ} = \phi_2^{\circ} = \phi^{\circ}$ since the diffusion and the

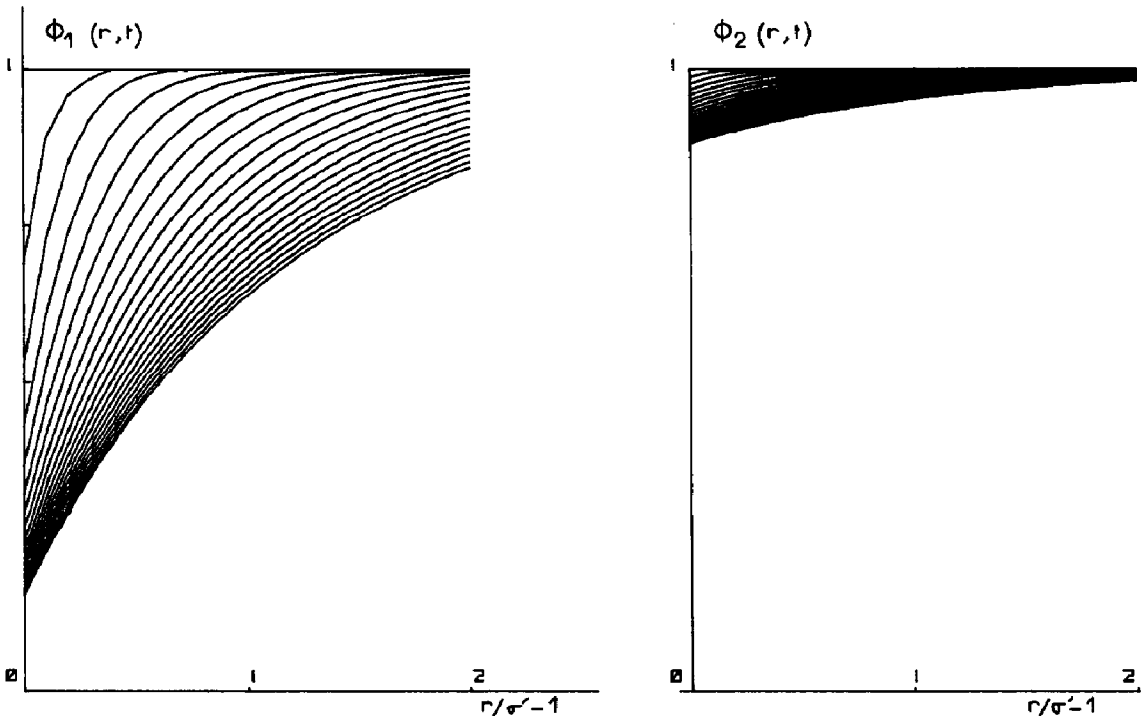
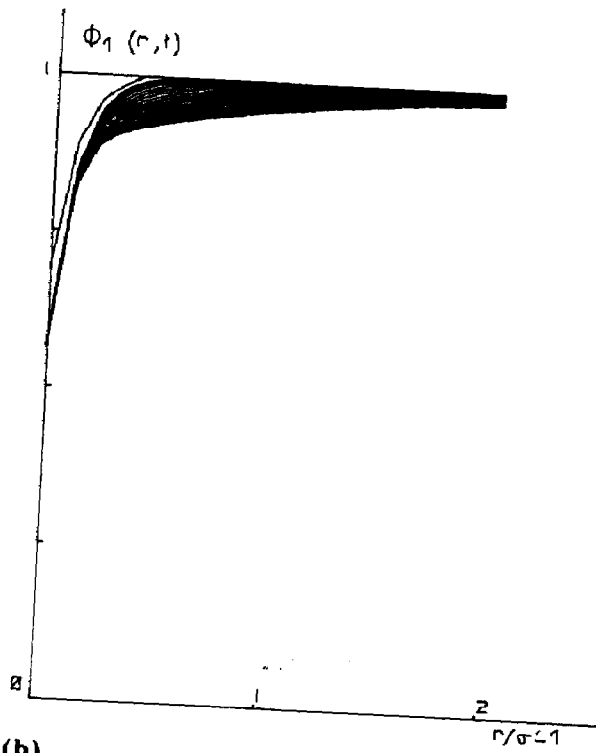
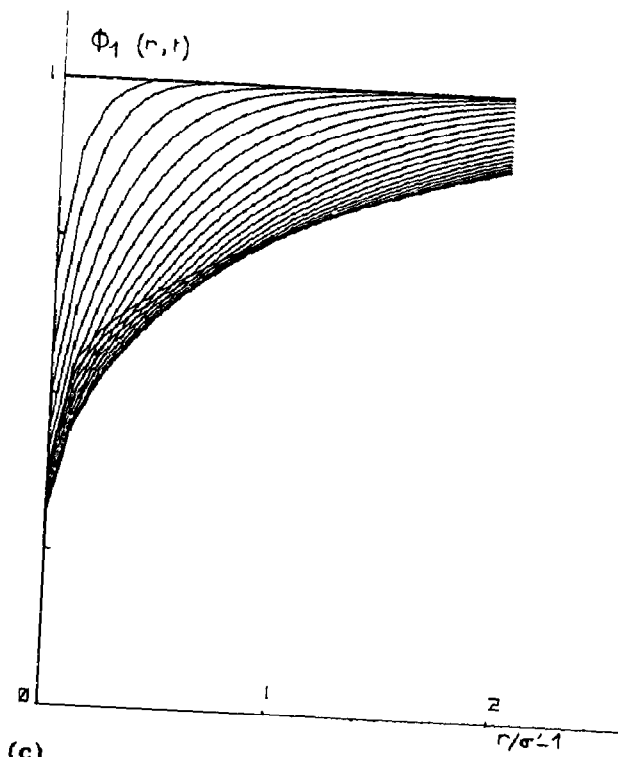
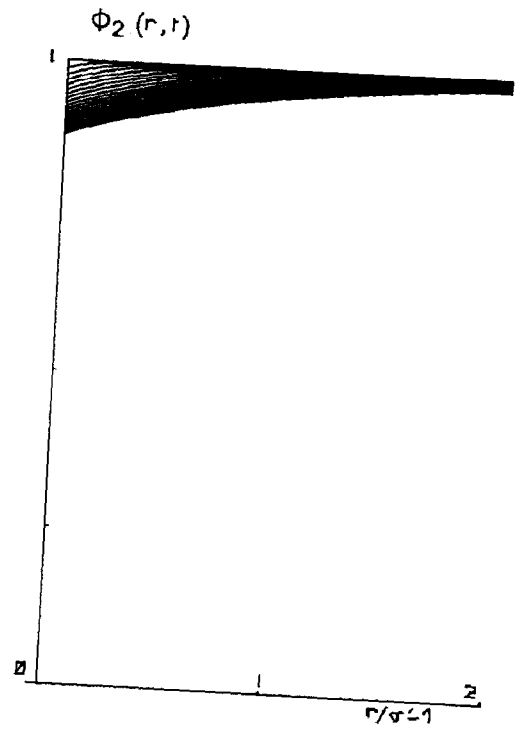


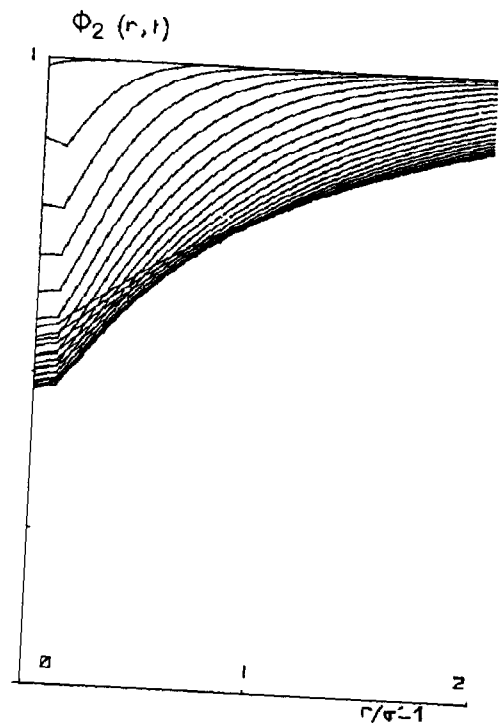
Fig. 5(a) (for caption see overleaf)

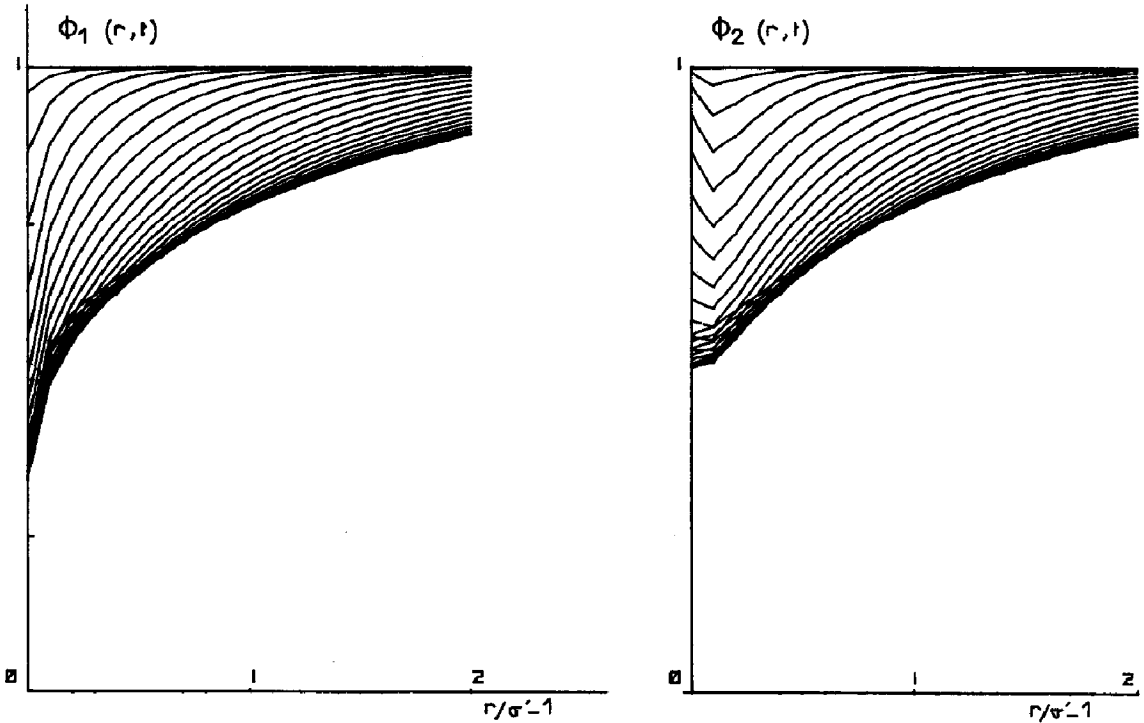


(b)



(c)





(d)

Fig. 5. Time evolution of the distribution function for $r > \sigma'$ (probability of formation of A_1 , $\alpha_1 = 0.4$; probability of formation of A_2 , $\alpha_2 = 0.6$; $\sigma' = 10 \text{ \AA}$; $D = 1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; $k_{10} = 0.5 \times 10^9 \text{ s}^{-1}$; $k_{20} = 10^9 \text{ s}^{-1}$; $\langle [B] \rangle = 0.1 \text{ mol l}^{-1}$; $k_{c1}/k_0 = 9$; $k_{c2}/k_0 = 0.25$): (a) $\sigma = 10 \text{ \AA}$, $k_{12} = k_{21} = 0$, $A_1 \not\rightleftharpoons A_2$; (b) $\sigma = 10 \text{ \AA}$, $k_{12} = 0$, $k_{21} = 0.25 \times 10^9 \text{ s}^{-1}$, $A_1 \rightleftharpoons A_2$; (c) $\sigma = 10 \text{ \AA}$, $k_{12} = k_{21} = 10^9 \text{ s}^{-1}$, $A_1 \rightleftharpoons A_2$; (d) $\sigma = 6 \text{ \AA}$, $k_{12} = k_{21} = 10^9 \text{ s}^{-1}$, $A_1 \rightleftharpoons A_2$. The distribution functions ϕ_1 and ϕ_2 are plotted for the following times (in nanoseconds): $t = 10^{-8} n^2$ for $n = 0 - 14$.

disappearance of B around A_1 and A_2 are identical. The system giving ϕ is then reduced to

$$\frac{\partial \phi}{\partial t} = D \Delta \phi$$

(28)

$$k_0 \sigma' \left(\frac{\partial \phi}{\partial t} \right)_{\sigma'} = N V_1 \frac{d\phi^0}{dt} + k_c \phi^0$$

The solution of such a system has already been carried out [3], leading to the following value* of $\phi^0(\tau)$ or $\phi(r, t)$ at distance σ' :

*In the case where $\alpha(\beta + 1) < \frac{1}{4}$, which is the usual case.

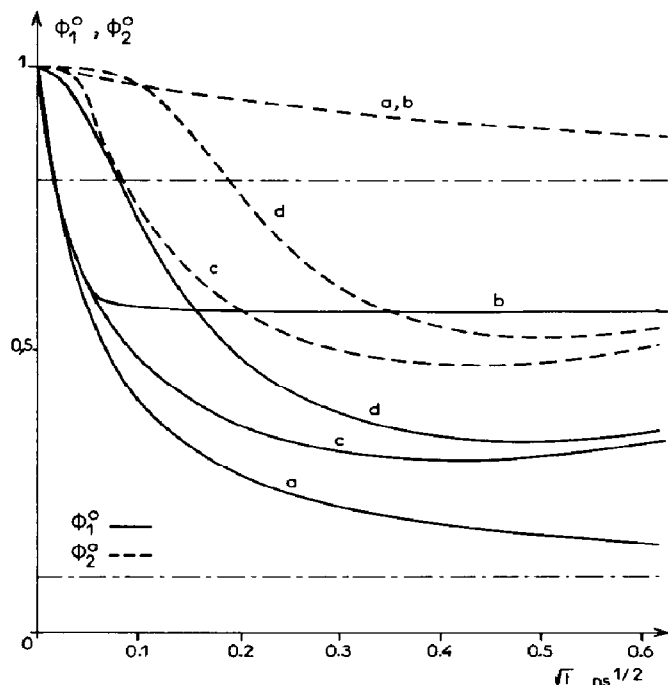


Fig. 6. Time evolution of ϕ_1^o and ϕ_2^o (values of the distribution functions ϕ_1 and ϕ_2 in the reacting range) under the same conditions as those given in Fig. 5.

$$\begin{aligned} \phi^o(\tau) = & \frac{1}{\beta + 1} - \frac{2\alpha\beta}{\gamma(1 + \gamma)} \exp\left\{\left(\frac{1 + \gamma}{2\alpha}\right)^2 \tau\right\} \operatorname{erfc}\left\{\left(\frac{1 + \gamma}{2\alpha}\right) \tau^{1/2}\right\} + \\ & + \frac{2\alpha\beta}{\gamma(1 - \gamma)} \exp\left\{\left(\frac{1 - \gamma}{2\alpha}\right)^2 \tau\right\} \operatorname{erfc}\left\{\left(\frac{1 - \gamma}{2\alpha}\right) \tau^{1/2}\right\} \end{aligned} \quad (29)$$

with $\gamma = \{1 - 4(\beta + 1)\alpha\}^{1/2}$ and where $\beta = k_c/k_o$, $\alpha = \frac{1}{3} \{1 - (\sigma/\sigma')^3\}$ and $\tau = Dt/\sigma^2$.

In particular, when $\alpha = 0$ we obtain the relation

$$\phi_1(\tau) = \frac{1}{\beta + 1} + \frac{\beta}{\beta + 1} \exp\{(\beta + 1)^2 \tau\} \operatorname{erfc}\{(\beta + 1) \tau^{1/2}\} \quad (30)$$

This relation is close to that proposed by Nemzek and Ware [5], by Owen [15] and by Collins and Kimball [16]. However, this expression corresponds to the case where $\sigma' = \sigma$. These authors assume $\sigma' > \sigma$, but do not take into account the accumulation of B corresponding to the term $NV_1(\partial\phi/\partial t)$.

For values of τ greater than about unity (*i.e.* t around 10^{-10} s in usual solvents) these relations reduce to

$$\phi^o(\tau) \approx \frac{1}{\beta + 1} \left\{ 1 + \frac{\beta}{\beta + 1} \frac{1}{(\pi\tau)^{1/2}} \right\} \quad (31)$$

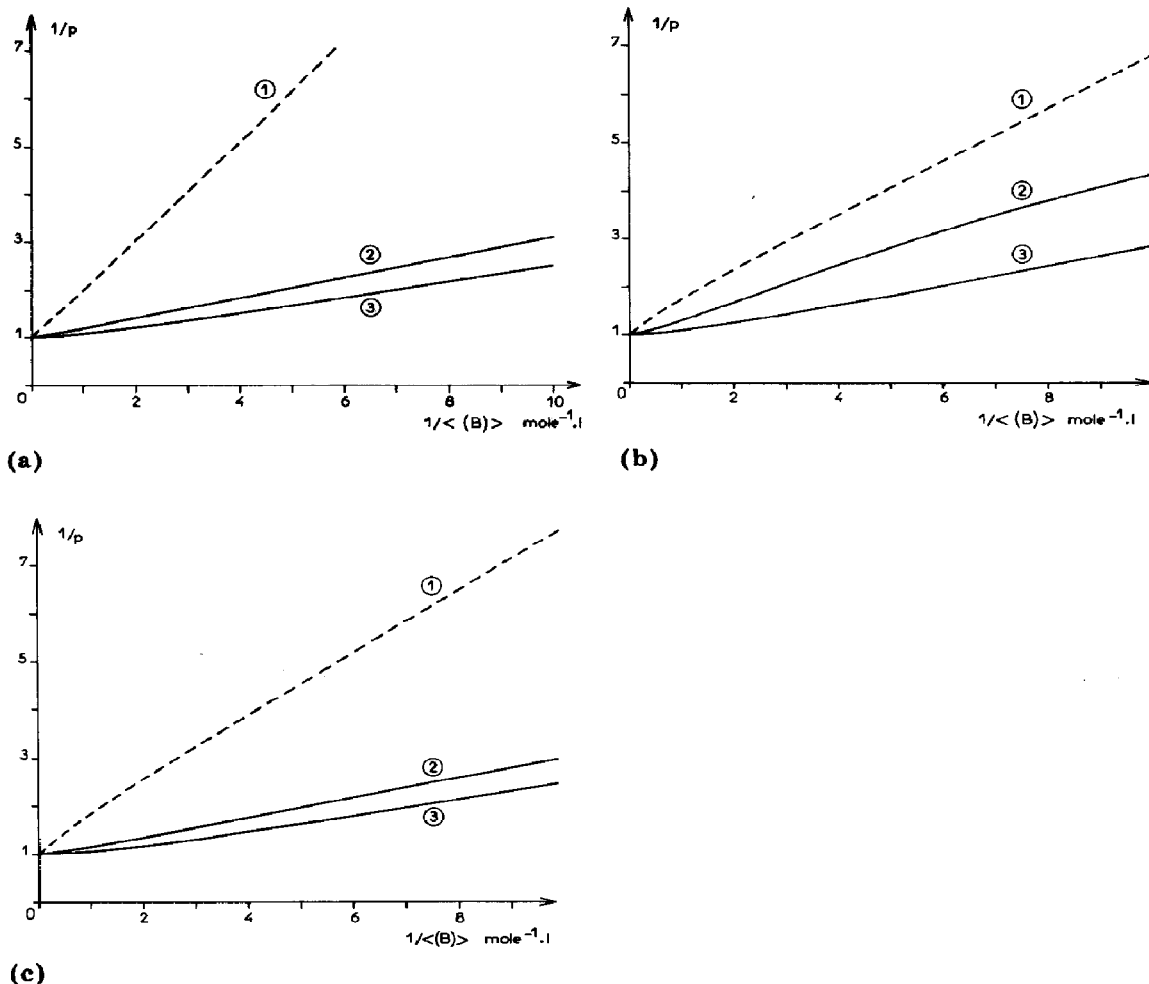


Fig. 7. Variations of the inverse of the yield p of transfer from A_1 and A_2 to B, with the inverse of the concentration $\langle B \rangle$ of the acceptor (probability of formation of A_1 , $\alpha_1 = 0.4$; probability of formation of A_2 , $\alpha_2 = 0.6$; $\sigma' = 10 \text{ \AA}$; $D = 0.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; $k_{10} = 0.2 \times 10^9 \text{ s}^{-1}$; $k_{20} = 0.8 \times 10^9 \text{ s}^{-1}$; $k_c/k_0 = 3$): (a) $A_1 \rightleftharpoons A_2$, $k_{12} = k_{21} = 0$ (relation (35)); (b) $A_1 \rightleftharpoons A_2$, $k_{12} = 0$, $k_{21} = 0.2 \times 10^9 \text{ s}^{-1}$ (relation (35)); (c) $A_1 \rightleftharpoons A_2$, $k_{12} = 0.8 \times 10^9 \text{ s}^{-1}$, $k_{21} = 0.2 \times 10^9 \text{ s}^{-1}$ (numerical solution). In each case curve 1 is drawn neglecting static quenching and non-stationary diffusion, curve 2 is drawn assuming $\sigma = \sigma' = 10 \text{ \AA}$ (no static quenching) and curve 3 is drawn taking into account both static quenching and non-stationary diffusion ($\sigma = 6 \text{ \AA}$).

3.2.2. Time evolution of $[A_1]$ and $[A_2]$ when $k_{c1} = k_{c2}$ and $k_{21} = 0$

The resolution of system (27) cannot be carried out analytically except in particular cases. However, a numerical solution can be obtained and leads to the results shown in Fig. 7.

In the case where $k_{21} = 0$, system (27) can be reduced and solved, leading to an approximate solution for the mean concentration of A_1 under constant excitation:

$$\frac{\langle [A_1] \rangle}{\langle [A_1] \rangle_{\langle [B] \rangle = 0}} \approx I_1(\lambda') \exp(-NV'_1 \langle [B] \rangle) \left(1 + \frac{k_0 k_c}{k_0 + k_c} \tau_1^\circ \langle [B] \rangle \right)^{-1} \quad (32)$$

where τ_1° represents the natural lifetime of A_1 ($1/\tau_1^\circ = k_{10} + k_{12}$) and

$$I_1(\lambda') = \int_0^\infty \exp(-a_1 u - \lambda'_1 u^{1/2}) du$$

with

$$a_1 = \frac{1}{\tau_1^\circ} + \frac{k_c k_0}{k_c + k_0} \langle [B] \rangle$$

and

$$\lambda'_1 = \frac{2\sigma'}{(\pi D \tau_1^\circ)^{1/2}} \frac{k_c k_0 \tau_1^\circ \langle [B] \rangle}{(k_c + k_0)^2} \left(1 + \frac{k_c k_0}{k_c + k_0} \tau_1^\circ \langle [B] \rangle \right)^{-1/2}$$

Also

$$\frac{[A_1]}{[A_1]^\circ} \approx \exp(-NV'_1 \langle [B] \rangle) \exp(-a_1 t - b t^{1/2}) \quad (33)$$

where $[A_1]^\circ$ represents $[A_1]$ at time $t = 0$ with

$$b = \frac{k_c^2 k_0}{(k_c + k_0)^2} \frac{2\sigma'}{(\pi D)^{1/2}} \langle [B] \rangle$$

From this simplified relationship the time evolution of A_2 can be calculated.

(1) In the case when $k_{12} = 0$

$$\frac{[A_2]}{[A_2]^\circ} \approx \exp(-NV'_1 \langle [B] \rangle) \exp(-a_2 t - b t^{1/2})$$

where $[A_2]^\circ$ represents $[A_2]$ at time $t = 0$ with

$$a_2 = \frac{1}{\tau_2^\circ} + \frac{k_c k_0}{k_c + k_0} \langle [B] \rangle$$

and $\tau_2^\circ = 1/(k_{20} + k_{21}) = 1/k_{20}$ in the present case.

(2) When $k_{12} \neq 0$

$$[A_2] = \frac{\exp(-NV'_1 \langle [B] \rangle)}{a_2 - a_1} [k_{12} [A_1]^\circ \exp(-a_1 t - b t^{1/2}) + \{(a_2 - a_1)[A_2]^\circ - k_{12} [A_1]^\circ\} \exp(-a_2 t - b t^{1/2})]$$

leading to

$$\frac{\langle [A_2] \rangle}{\langle [A_2] \rangle_{\langle [B] \rangle = 0}} \approx \frac{1}{\tau_2^\circ (\tau_1^\circ k_{12} [A_1]^\circ + [A_2]^\circ)} \frac{\exp(-NV'_1 \langle [B] \rangle)}{a_2 - a_1} \times \left\{ \frac{k_{12} [A_1]^\circ}{a_1} I(\lambda'_1) + \frac{(a_2 - a_1)[A_2]^\circ - k_{12} [A_1]^\circ}{a_2} I(\lambda'_2) \right\} \quad (34)$$

with

$$\lambda'_2 = \frac{2\sigma'}{(\pi D\tau_2^\circ)^{1/2}} \frac{k_c^2 k_0 \tau_2^\circ \langle [B] \rangle}{(k_c + k_0)^2} \left(1 + \frac{k_c k_0}{k_c + k_0} \tau_2^\circ \langle [B] \rangle \right)$$

and

$$I(\lambda'_2) = \int_0^\infty \exp(-a_2 u - \lambda'_2 u^{1/2}) du$$

3.2.3. Yield of sensitization

In the case of A_1 this yield is readily expressed using relation (22)

$$p_1 = 1 - I(\lambda'_1) \exp(-NV_1' \langle [B] \rangle) \left(1 + \frac{k_0 k_c}{k_0 + k_c} \tau_1^\circ \langle [B] \rangle \right)^{-1}$$

However, in the case of A_2 the calculation is more complicated. We define the probability at time $t = 0$ as $p_{2,s}$. Then

$$p_{2,s} = 1 - \exp(-NV_1' \langle [B] \rangle)$$

We define the probability at time $t > 0$ as $p_{2,d}$. Then

$$p_{2,d} = 1 - \frac{\langle [A_2] \rangle}{\langle [A_2] \rangle_{\langle [B] \rangle = 0}} - p_{2,s}$$

This leads to the following expression of the total sensitization yield by A_1 and A_2 :

$$\begin{aligned} p_{A_1, A_2 \rightarrow B} = & \alpha_1 \left\{ 1 - \frac{I(\lambda'_1) \exp(-NV_1' \langle [B] \rangle)}{a_1 \tau_1^\circ} \right\} + \\ & + \alpha_2 \left(1 - \{ \exp(-NV_1' \langle [B] \rangle) \} \times \right. \\ & \times \frac{1}{\tau_2^\circ (\tau_1^\circ k_{12} \alpha_1 + \alpha_2)} \frac{\tau_1^\circ \tau_2^\circ}{\tau_1^\circ - \tau_2^\circ} \times \\ & \left. \times \left[k_{12} \alpha_1 \frac{I(\lambda'_1)}{a_1} + \{ (a_2 - a_1) \alpha_2 - k_{12} \alpha_1 \} \frac{I(\lambda'_2)}{a_2} \right] \right) \end{aligned} \quad (35)$$

This complicated relationship was used to draw the curves shown in Fig. 7 which show the complex influence of $\langle [B] \rangle$ on the yield of sensitization. Taking into account the experimental accuracy and the number of parameters involved, it does not seem likely that this type of experiment for the determination of p_1 , p_2 , τ_1° , τ_2° , σ' etc. can be easily exploited. Then, as we have pointed out in the introduction, high concentrations of acceptor B are often required and it is often necessary to look for very effective reactions the rates of which are diffusion controlled, in order to characterize excited states of short lifetime. Thus, we have shown how difficult it is to obtain specific parameters from experimental data when two excited donor states

A_1 and A_2 interact and have a short lifetime (about 1 ns for example). In contrast, if the lifetimes of A_1 and A_2 are long enough (much more than 10 ns in usual solvents) linear relationships such as those presented in ref. 1 can be successfully used.

3.2.4. Case where there is no exchange between A_1 and A_2

In this particular case, we have therefore $k_{21} = k_{12} = 0$ and the kinetic treatment of the sensitization process can be carried out. This has been done in the case of reactions with diffusion-controlled kinetics [4, 13, 14]. Relationship (35) yields

$$P_{A_1, A_2 \rightarrow B} = \alpha_1 + \alpha_2 - \exp(-NV'_1 \langle [B] \rangle) \left\{ \frac{\alpha_1 I(\lambda'_1)}{a_1 \tau_1^0} + \frac{\alpha_2 I(\lambda'_2)}{a_2 \tau_2^0} \right\} \quad (36)$$

which is illustrated in Fig. 7.

4. Conclusions

We have shown in this work the tricky problems that arise when the experimenter wishes to carry out a complete kinetic treatment of the sensitization reaction of a species B by two electronically excited species A_1 and A_2 which interact. When the lifetime of these latter species is relatively long (much more than 10 ns in usual solvents) the relationships reported in ref. 1 remain valid as long as the concentration of acceptor is low enough to prevent static quenching. In contrast, for shorter lifetimes of the donors, or for solvents of higher viscosity, non-stationary diffusion is no longer negligible and static quenching occurs. These phenomena alter greatly the kinetic relationships describing the reacting system.

Acknowledgment

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Nomenclature

A	reactive species
A^* , A_1 , A_2	excited states of a reactive molecule
$\langle [A_1] \rangle$, $\langle [A_2] \rangle$	mean concentrations of A_1 and A_2 under continuous excitation
$\langle [A_1] \rangle \langle [B] \rangle = 0$, $\langle [A_2] \rangle \langle [B] \rangle = 0$	mean concentrations of A_1 and A_2 in the absence of B
B	reactive species
$[B(r, t)]$, $[B_1(r, t)]$, $[B_2(r, t)]$	local concentrations of B molecules around A or A^* , A_1 and A_2 respectively
$[B^\sigma]$, $[B_1^\sigma]$, $[B_2^\sigma]$	local concentrations of B molecules between σ and σ' relative to A or A^* , A_1 and A_2

$\langle [B] \rangle$	mean concentration of B molecules in the bulk of the solution
D, D_1, D_2	diffusion coefficients relative to A or A*, A ₁ and A ₂
\mathcal{G}	time evolution operator
J	flow of particles
$k(r)$	rate constant of the reaction of one molecule A with one molecule B
k_0	diffusional rate constant $4\pi N\sigma'D$
k_c, k_{c1}, k_{c2}	bimolecular chemical rate constant of the reaction of B with A or A*, A ₁ and A ₂
$k_a(t)$	apparent rate constant of reaction
$k, k_{10}, k_{11}, k_{20}, k_{21}$	rate constants of the disappearance and formation of A or A*, A ₁ and A ₂ in the absence of B
N	Avogadro's number
$N_1(t), N_2(t)$	number of molecules A ₁ and A ₂ at time t
p, p_1, p_2	probabilities of photosensitization from A or A*, A ₁ and A ₂
$p_{A_1, A_2 \rightarrow B}$	probability of sensitization of B* from both the A ₁ and A ₂ states
r	distance between A or A*, A ₁ and A ₂ and B
t	time
V_1	reaction volume
V_1'	apparent reaction volume
∇^2	laplacian operator

Greek symbols

α	coefficient equal to $\frac{1}{3} \{1 - (\sigma/\sigma')^3\}$
α_1, α_2	probabilities of formation of the two excited states A ₁ and A ₂
β	coefficient equal to k_c/k_0
γ	coefficient equal to $\{1 - 4(\beta + 1)\alpha\}^{1/2}$
σ	encounter distance
σ'	limit of the "reaction volume"
$\phi(r, t)$	$[B(r, t)]/\langle [B] \rangle$
ϕ, ϕ_1, ϕ_2	configurational distribution functions relative to A or A*, A ₁ and A ₂
$\phi^\circ, \phi_1^\circ, \phi_2^\circ$	values of $\phi(r, t)$ between σ and σ' around respectively A or A*, A ₁ and A ₂

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