

# Cage Effect Dynamics in the Liquids

Igor V Khudyakov\*

Chemistry Department, Columbia University, New York

\*Corresponding author: Igor V Khudyakov, Chemistry Department, Columbia University, New York

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## ABSTRACT

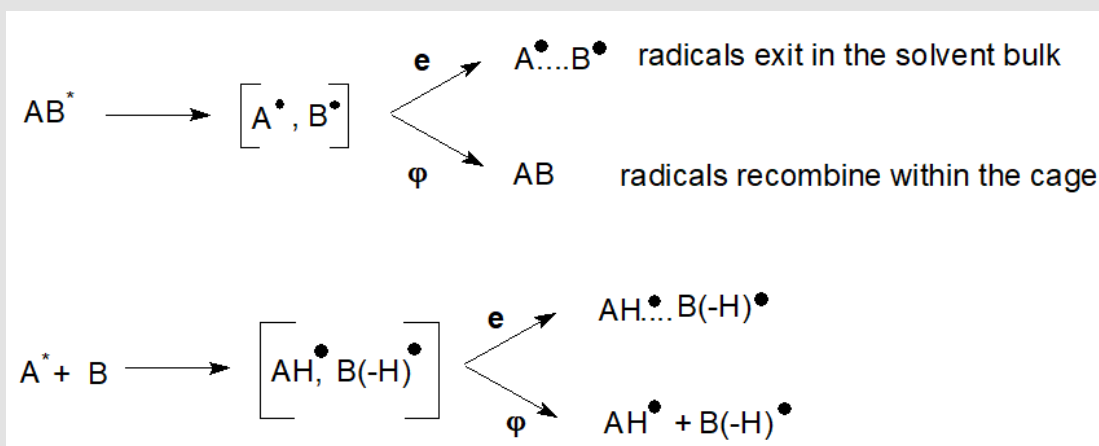
The cage effect and cage escape are explained concisely. An example of cage dynamics is presented. A commonly used simple exponential model of a cage only roughly approximates theoretical and experimental cage dynamics and effects.

**Keywords:** Cage Effect; Cage Escape; Kinetics of Geminate Recombination and Dissociation

## Introduction

The cage effect is an important phenomenon accompanying free radical reactions in the liquid phase. Researchers have studied cage effect values under thermolysis and photolysis of organic molecules into free radicals since the 1930s (see, for review [1-8]). The development of time-resolved techniques with high resolution allowed studying not only cage effect values but also the dynamics of cage effect or kinetics of geminate recombination of photoinduced radicals. We denote cage value as  $\phi$  and cage escape value as  $e$ .  $\phi(e)$  is the fraction of radicals or other reactive species generated pairwise that react in (escape from) the cage. Scheme 1 below presents a couple of generic examples. The word "effect" has been used for 90 years and

does not make sense when one studies reactions in solution [7]. It has a historical meaning. We may imagine any couple of non-reactive solvent molecules in proximity. Other solvent molecules surround them, and they are in a solvent cage. They participate in contact with each other before separation. For these two molecules,  $\phi = 0$ . In this brief note, we consider only the formation of neutral free radicals obtained during pico- or nanosecond flash photolysis. We do not aim to review all the available publications but only to illustrate important points and clear misconceptions. Radicals enclosed in square brackets in Scheme 1 are commonly referred to as geminate G-RP. Free F-RP is generated by random encounters of free radicals in the solvent bulk.



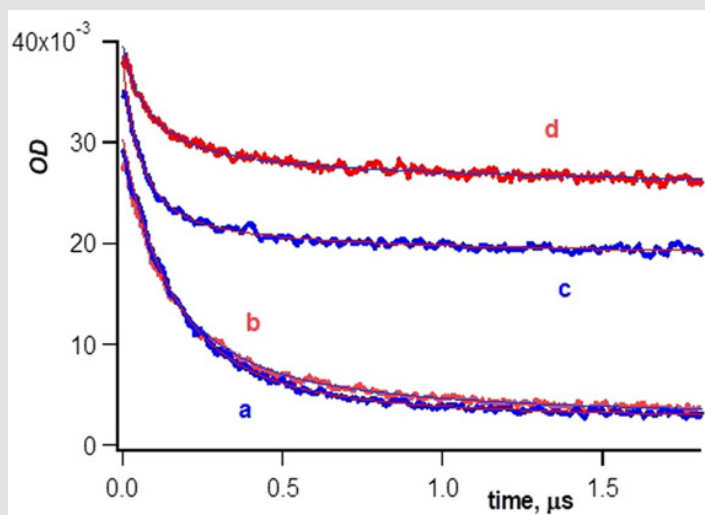
**Scheme 1:** The molecule  $AB^*$  dissociates in the excited singlet or triplet state, forming a radical pair (RP). A bimolecular reaction between a photoexcited molecule and a quencher can involve a hydrogen atom transfer and result in RP. Reactions between radicals, which we call here recombination; it can be a disproportionation or electron transfer between radicals.

### Kinetics of Geminate Recombination

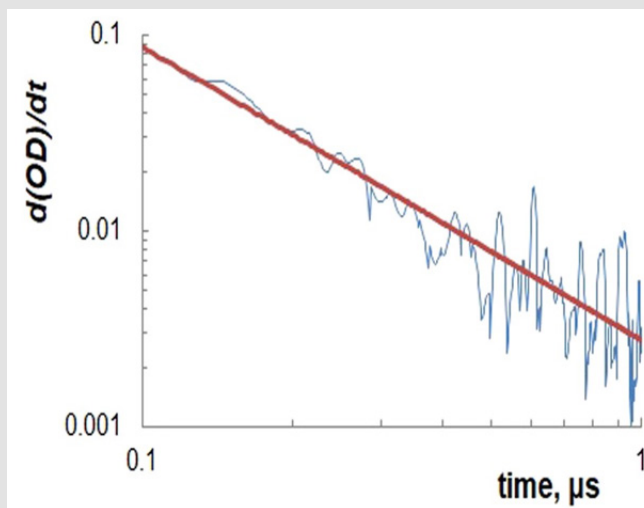
It is widely believed that kinetic curves observed during ps photolysis of molecular iodine in carbon tetrachloride and hexadecane, performed in 1974, are the first experimental observation of geminate recombination of iodine atoms [9]. The kinetics lasts  $\sim 100$  ps. The publication [9] has hundreds of citations, and the kinetic curves of [9] are included in the review articles and a book, see e.g. [1,4,8]. (For a fairness's sake, it is necessary to mention that refs [4,8] present reservations about assigning the observed picosecond kinetics to geminate recombination.) It was proved that cage recombination/cage dissociation of iodine atoms lasts 5 ps, and the observed curves are vibrational relaxation of  $I_2$  and not a geminate recombination [10,11]. The kinetics of geminate recombination were experimentally observed for the first time with aromatic neutral free radicals in viscous media only in 1980 [12]. Identical radicals were produced via ns flash photolysis of their dimer (refer to Scheme 1, top equation,  $A=B$  in [12]). For more details, refer to [12]. Much better experimental results on geminate recombination were obtained with ns flash photolysis of benzophenone or its simple derivatives in the presence of high concentration methyl phenols [13-15]. The viscous solvent glycerol was used. The second equation in Scheme 1 shows benzophenone's excited triplet state ( $A^*$ ) reacting with phenol (B). That way, we managed to separate in time the cage formation, cage dynam-

ics, and recombination in the solvent bulk of neutral radicals that escaped the cage. See Figure 1 as an example: Figure 1 demonstrates that applying a moderate magnetic field at certain temperatures/viscosities results in an increase of  $e$ . Most publications present simple expressions for  $e$  and  $\phi$  as  $e = \frac{k_d}{k_d + k_r}$  and  $\phi = \frac{k_r}{k_d + k_r}$  suggested in the 1960s.  $k_d$  is the rate constant of diffusion from the cage, and  $k_r$  is the rate constant of cage reaction. The reactions are first-order. Some publications omit the dimensions of these rate constants, e.g. [2]. Such publications use an approximate exponential model of the cage. The "tail" of the RP kinetic curve decay follows a  $c \sim t^{-1/2}$  kinetic law instead of  $c \sim \exp[-(k_r + k_d)t]$ , as confirmed experimentally [13-15]. Figure 2 presents the experimental proof of the latter statement. Rate of recombination or  $dc/dt \sim d(OD)/dt \sim t^{-3/2}$ , see Figure 2:

Theoretical studies of cage dynamics agree with the relevant experimental studies of a system of ketyl and phenoxyl [13,15], like those presented in Figure 1. There is an experimental way to distinguish between geminate RP and radicals in the solvent bulk in experiments with transient spectroscopy. The measured  $\phi$  values should not depend upon the initial concentration of RP  $[RP]_0$  (or a laser pulse energy). The rate of decay of radicals in the solvent bulk is directly proportional to the initial concentration of radicals  $[R]_0$ . That rate is directly proportional to  $[R]_0^2$ , if radicals in RP are identical and decay only by self-termination. It is assumed that radicals in RP are generated in the first or second coordination sphere (separated by a solvent molecule) [4, 15].



**Figure 1:** Decay kinetics of the transient absorption at  $\lambda = 555$  nm obtained under photoexcitation of 4,4'-dimethylbenzophenone (5 mM) in glycerol in the presence of 4-methylphenol (1.5M). The observed transient is ketyl free radical. a and c - experiments conducted in Earth's magnetic field; b and d - experiments conducted in an external magnetic field,  $B = 0.2$  T. The temperature of the solution was 273 (a and b) and 313 K (c and d). Thin solid lines are fitting into the suggested theory [15]. The radicals in the solvent bulk decay much more slowly and follow the second-order law.  $OD$  is optical density; all data are from [15].



**Figure 2:** The plot of the first derivative of  $OD$   $d(OD)/dt$  vs time at  $t \geq 0.1 \mu s$  in logarithmic coordinates for a curve "a" taken from Figure 1. The line is the linear fit of the experimental data (the slope is  $-3/2$ ) [15].

## Conclusion

The simulation of the cage effect with macroscopic balls performed in the 1930ies [1] interests a historian of science. Modern simulation of molecular dynamics (MD) allows analysis of the cage dynamics accounting for radical-solvent potentials, packing of solvent molecules around pair (coordination number), cage restoring forces generated by solvent, and particle residence lifetimes, relative masses of solvent and solute, and other cage variables, see e.g. [16,17]. This

study on the cage effect is a valuable addition to the theoretical calculations [13,15]. In summary, the initial phase of geminate recombination kinetics follows an exponential law  $c \sim \exp(-k.t)$ , while the recombination tail follows the law  $c \sim t^{-1/2}$ . Theoreticians combined these two extremes into one analytical formula [14,15]. The cage effect is of practical importance in chemistry. Chemists expect the lowest possible  $\Phi$  during thermo- or photoinitiation of free-radical polymerization and the highest  $\Phi$  during free-radical photodegradation of coatings and polymers outdoors.

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Igor V Khudyakov. *Biomed J Sci & Tech Res*



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