

A Modern Approach to the Cage Effect in Liquids



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Abstract

The cage effect and cage escape are briefly described. An example of cage dynamics is presented. An enhancement in charge separation of radical-ions is suggested.

Keywords: Cage Effect; Cage Escape; Charge Separation

Introduction

The cage effect and escape have attracted considerable interest in the last few years [1-4]. Below, we provide brief clarifying comments on this subject. We denote cage value as φ and cage escape value as e . φ (e) is the fraction of radicals or other reactive species generated pairwise which react in (escape from) the cage Scheme 1. The reaction of IRP in the cage is back electron transfer (BET). The cage effect was reviewed in several articles [2,4-9]. 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 contacts with each other before separation. For these two molecules $\varphi = 0$.

Cage Effect Dynamics

The kinetics of cage dynamics (recombination and escape), including BET, are very complex and have been the subject of many theoretical works [9-13]. The kinetics of geminate recombination was experimentally observed for the first time with aromatic neutral free radicals in viscous media only in 1980 [14]. Most publications present simple expressions for e and φ as $e = k_d/(k_d+k_r)$ and $\varphi = k_r/(k_d+k_r)$ 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 and of BET in particular. Moreover, many publications even avoid presenting the dimensions of these rate

constants [2,15,16]. Apparently, these are the first-order reactions (s^{-1}) [17], and such publications use an approximate exponential model of the cage. It is enough to mention that the "tail" of decay of the RP kinetic curve follows not $\sim \exp[-(k_r+k_d)t]$ but $\sim t^{-1/2}$ kinetic law, which was confirmed experimentally [18]. Still, k_r and k_d are of practical value for the analysis of the experiment. We managed to separate in time the cage formation, cage dynamics, and recombination in the solvent bulk of neutral radicals that escaped the cage Figure 1.

Theoretical studies of cage dynamics agree with the relevant experimental studies of a system of ketyl and phenoxyl [20,21], like those presented in Figure 1. Many theoretical works are devoted to the generation and decay of IRP [9-13]. However, to our knowledge, there are only a few experimental observations of the kinetics of IRP photogeneration and decay [22,23]. It is obvious that $\varphi + e = 1.0$ [5]. A study of $\varphi = \varphi(t)$ gives the info on $e=e(t)$ and vice versa. In many chemical processes, it is important to have low φ . Such reactions are photoinitiation of free radical reactions in solution and electron transfer to create free radical-ions in the solvent bulk. It was demonstrated that solvent viscosity, in most cases, has a dominant effect preventing radical exit of the cage [5,6-8,17,18-21].

By definition, the quantum yield of Φ_p of a product of photochemical reaction possibly proceeding via steps of intermediates is:

$$\Phi_p = \frac{\text{moles of the formed product of interest}}{\text{einstains of of absorbed photoactive light}}$$

In our case, the product of interest is a transient radical in the solvent bulk whose absorption (concentration) can be measured by transient spectroscopy. (einstein is a mole of light quanta). Evaluation of Φ_p usually requires tedious actinometry

measurements. However, a method was found to measure $\Phi_p = e$ by comparison of the measured concentration of the photoexcited sensitizer A^* (Scheme 1), degree of quenching of A^* , and initial concentration of the radical-ion exited in the solvent bulk. The extinction coefficients of transients are known. An enormous effort is dedicated to the measurements of e of IRP. Almost all the known values of e were nicely compiled in [2].

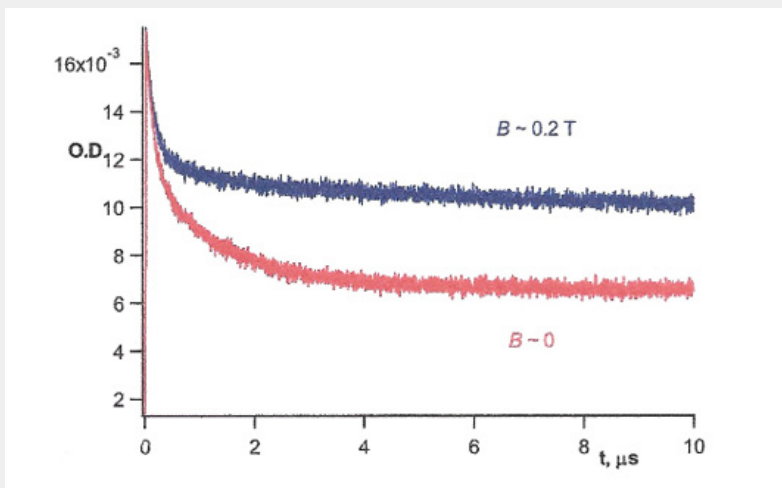
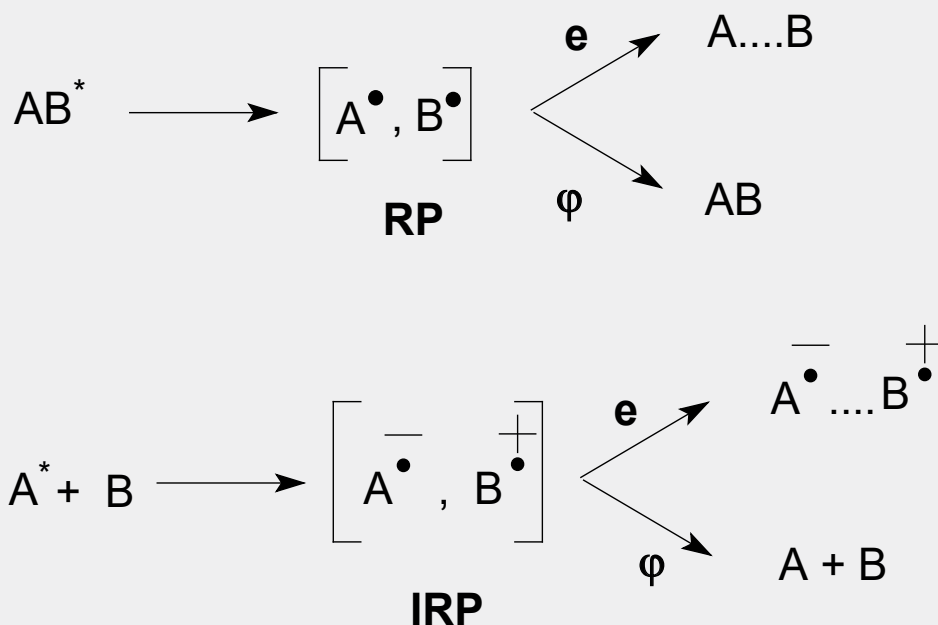


Figure 1: Geminate recombination of a triplet pair of benzophenone ketyl free radical and phenoxyl radical in elastomer. The reaction was performed in the Earth's magnetic field ($B \sim 0$) and a magnetic flux density $B \sim 0.2$ T. An absorption of ketyl radical was monitored. A quasi plateau is an absorption of ketyl radicals in the solvent bulk. The radicals in the solvent bulk decay much slower and follow the second-order law [19]. A similar performance was observed in the viscous liquid [18].



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 lead to an ion-radical pair (IRP).

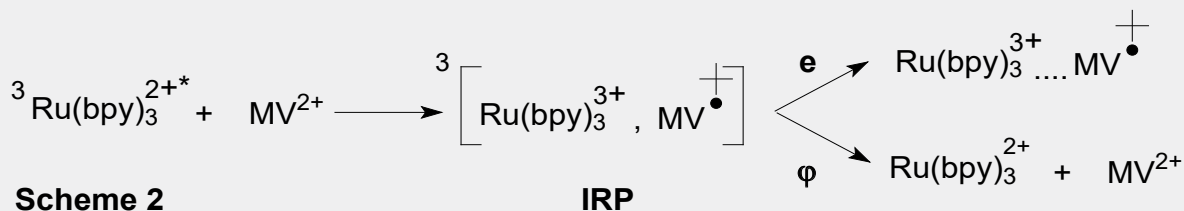
There is an experimental way to distinguish between geminate RP (IRP) and radicals in the solvent bulk in experiments with transient spectroscopy. The measured ϕ -values should not depend upon the initial concentration of RP $[RP]_0$ (or a laser pulse energy). The rate of decay of radicals in the solvent 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) [6].

Tris(2,2'-bipyridyl)ruthenium (II) $Ru(bpy)_3^{2+}$ and N,N'-dimethylviologen MV^{2+}

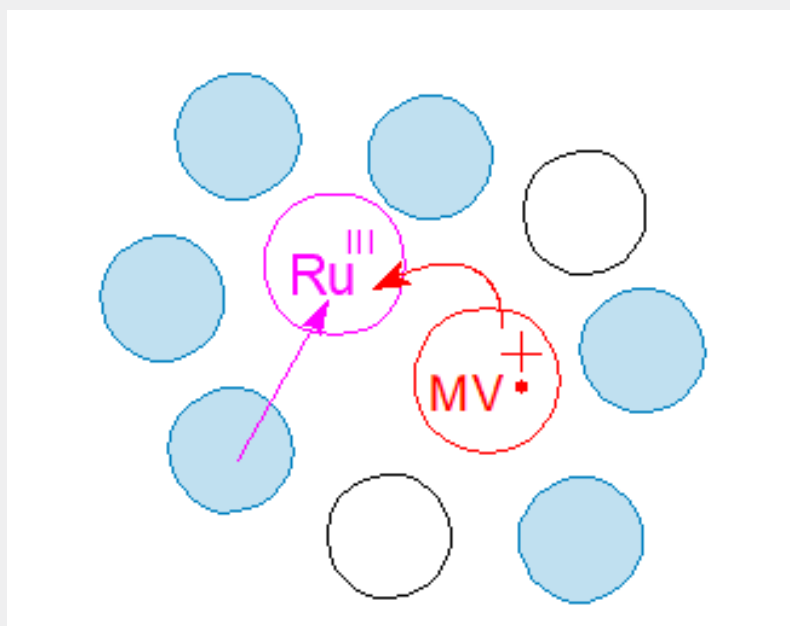
The main trend in the utilization of visible light is the photoexcitation of transition metal compounds in the presence of acceptors. An excited state is quenched by a donor or acceptor, leading to the formation of a radical-cation and radical-anion in the solvent bulk. Another option is the formation of a positively

charged transition metal compound and a positively charged radical cation. Further reactions of generated ions in the solvent bulk are expected eventually lead to the evolution of dihydrogen. In any case, we deal with charge separation. The most widely studied system is $Ru(bpy)_3^{2+}$ and MV^{2+} in aqueous or other polar solvents [15-17].

IRP is formed with a probability of almost unity in the presence of mM concentration of MV^{2+} in water or a polar inert solvent in experiments with an ns laser flash photolysis. The disappointing fact is that BET is very efficient, and the IRP has a typical value of $e \sim 0.25$ [2,16]. There are a couple of reasons for that (high exothermicity of BET, insufficient spin prohibition in the presence of a "heavy" nucleus of Ru). In addition, IRP has lower Coulomb repulsion in the case of BET (3x1) than the same repulsion under the generation of IRP (2x2) Scheme 2. We propose the use of a very high concentration of reducing agent (D), which can be used as a solvent or as a cosolvent Scheme 3.



Scheme 2



Scheme 3: Pictorial presentation. Photogenerated Ru^{III} oxidizes donor molecules (D, blue spheres) and competes with BET. White spheres are inert in this process solvent molecules, e.g., water or acetonitrile. The direction of the arrows demonstrates the direction of electron transfer.

Such sacrificial D such as EDTA and triethanolamine (TEOA) were suggested [15,16]. We suggest 2-aminoethan-1-ol (ethanolamine) as a solvent or cosolvent. Hydrophilic liquid thiols like 2-sulfanylethan-1-ol (2-mercaptoethan-1-ol) may play the same role. It was estimated that when a scavenger is in a high concentration of ~ 1 M, it reacts with radicals in the primary cage [4,5]. It is a task to find experimentally suitable D that does not produce colored products under oxidation, demonstrates good solubility of the reagents being a solvent or cosolvent, and ideally produces a useful product of their oxidation. In this note, we do not consider the organic triplet sensitizers accepting the energy of $\text{Ru}(\text{bpy})_3^{2+}$ [16].

It is observed in laser flash photolysis experiments quenching of $\text{Ru}(\text{bpy})_3^{2+}$, the appearance of MV^+ in a microsecond and sub-microsecond time scale [15-17]. However, the dynamics of this IRP are not observed due to the very low concentration of IPR. IRP is an intermediate product (Scheme 2). Semi-quantitative estimations of k_d and k_r demonstrate that the lifetime of this IRP is $\tau = 1 / (1 \times 10^9 + 1.9 \times 10^9) = 0.5$ ns even in viscous ethylene glycol [17]. Running the same reaction in micelles allows observation of the formation and decay of IRP, but the radical-ions practically do not leave a micelle [24].

Conclusion

The simulation of the cage effect with macroscopic balls performed in the 1930ies [2] 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 [25,26].

References

- Wang C, Li H, Bürgin TL, Wenger OS (2024) Cage escape governs photoredox reaction rates and quantum yields. *Nature Chem* 16: 1151-1159.
- Goodwin MJ, Dickenson JC, Ripak A, Deetz AM, McCarthy JS, et al. (2024) Factors that impact photochemical cage escape yields. *Chem Rev* 124(11): 7379-7464.
- Ripak A, Vega Salgado AK, Valverde D, Cristofaro S, de Gary A, et al. (2024) Factors controlling cage escape yields of closed and open shell metal complexes in bimolecular photoinduced electron transfer. *ChemRxiv*: p1-12.
- Sarver P (2020) Radical cage effects.
- Koenig T, Fischer H (1973) Cage effects. In: *Free Radicals*, Kochi J (Ed.), Wiley: New York, U.S.A, pp.164.
- Khudyakov IV, Yakobson BI (1984) Influence of the solvent viscosity on cage effect. *Russ J Gen Chem* 54: 3.
- Khudyakov IV, Levin PP, Efremkin AF (2019) Cage effect under photolysis in polymer matrices. *Coatings* 9(2): 111.
- Khudyakov IV (2013) Transient free radicals in viscous solvents. *Res Chem Inter* 39: 781-804.
- Burshtein AI (2004) Non-Markovian theories of transfer reactions in luminescence and chemiluminescence and photo-and electrochemistry. *Adv Chem Phys* 129: 105.
- Mozumder A (1968) Theory of neutralization of an isolated ion pair: application of the method of prescribed diffusion to random walk in a Coulomb field. *J Chem Phys* 48: 1659-1665.
- Feskov SV, Ivanov AI (2021) Short time dynamics of radical ion pairs produced by photoinduced electron transfer in solution: The magnetic field effect. *Appl Magn Res* 53: 745-761.
- Krissinel EB, Burshtein AI, Lukzen NN, Steiner UE (1999) Magnetic field effect as a probe of distance-dependent electron transfer in systems undergoing free diffusion. *Mol Phys* 96(7):1083-1097.
- Burshtein AI (1999) Contact and remote ion radicals formation and recombination. *Chem Phys* 247(2): 275-291.
- Khudyakov IV, Kiryukhin Yu I, Yasmenko AI (1980) Kinetics of geminate recombination of aromatic free radicals. *Chem Phys Lett* 74(3): 462-466.
- Hoffman MZ (1988) Cage escape yields from the quenching of $\text{Ru}(\text{bpy})_3^{2+}$ by methylviologen in aqueous solution. *J Phys Chem* 92(12): 3458-3464.
- Olmsted III J, Meyer TJ (1987) Factors affecting cage escape yields following electron-transfer quenching. *J Phys Chem* 91(6): 1649-1655.
- Wolff HJ, Burher D, Steiner UE (1995) Spin-orbit coupling controlled spin chemistry of $\text{Ru}(\text{bpy})_3^{2+}$ photooxidation: Detection of strong viscosity dependence of in-cage backward electron transfer rate. *Pure & App Chem* 67(1): 167.
- Levin PP, Khudyakov IV, Kuzmin VA (1989) Geminate recombination kinetics of triplet radical pairs in glycerol: magnetic field effect. *J Phys Chem* 93(1): 208-214.
- Levin PP, Efremkin AF, Khudyakov IV (2017) Benzophenone as a photoprobe of polymer films. *Chem Phys* 495: 23-28.
- Khudyakov IV, Zharikov AA, Burshtein AI (2010) Cage effect dynamics. *J Chem Phys* 132(1): 014104.
- Levin PP, Shushin AI, Khudyakov IV (2019) Ketyl-phenoxy triplet radical pair in glycerol: Magnetic field effect and cage kinetics in terms of the two-state model. *J Chem Phys* 151(21): 214503.
- Werne HJ, Staerk H, Weller A (1978) Solvent, isotope, and magnetic field effects in the geminate recombination of radical ion pairs. *J Chem Phys* 68(5): 2419-2426.
- Mataga N, Asahi T, Kanda Yu, Okada T (1988) The bell-shaped energy gap dependence of the charge recombination reaction of geminate radical ion pairs produced by fluorescence quenching reaction in acetonitrile solution. *Chem Phys* 127(1-3): 249-261.
- Turro NJ, Khudyakov IV, Gopidas KR (1992) A laser flash photolysis study of magnetic field effects in photoinduced electron transfer between $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{N,N}'$ -dimethylviologen in micellar solutions. *Chem. Phys* 162: 131-143.
- Moro GJ, Nordio PL, Noro M, Polimeno AJ (1994) A cage model of liquids supported by molecular dynamics simulations. I. The cage variables. *Chem. Phys.*, 101(1): 693-702.
- Pestrayev LM (2018) Molecular dynamics simulation of the cage effect in a wide packing fraction range. *Russ. J Phys Chem A* 92: 1321-1331.



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