Initial Radical Separation after Photolysis of 2,2′-Azobis(isobutyronitrile) (AIBN) in Solution: Modeling the Primary Cage Effect for Polar Radicals

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Pro memoriam Hanns Fischer from a former Ph.D. student, a long-standing senior assistant, and a multiple guest of his former research group

There is a contradiction as to the initial spatial separation r_i of the two transient 2-cyanoprop-2-yl radicals ($Me_2\dot{C}-CN$) formed by flash photolysis of 2,2′-azobis(isobutyronitrile) (AIBN) in solvents of various viscosities. The cage effect, expressed in terms of the in-cage termination probability of the resulting radicals, is predicted correctly by classical *Langevin* models assuming a decrease of r_i with increasing viscosity. However, the electron-spin polarization of the radicals escaping the primary cage clearly indicates that the initial separation distance r_i is independent of the solution viscosity. This obvious discrepancy can be reconciled by accounting for the strong electric dipole moments of these radicals and the resulting inter-radical dipole–dipole interaction potential.

We propose a primary-caging model for polar radicals in solution based on an attractive inter-radical mean-force potential. The model is applied to the flash photolysis of AIBN and shown to describe properly the viscosity dependence of both the in-cage termination probability (cage effect) and the electron-spin polarization of the escaping 2-cyanoprop-2-yl radicals.

Introduction. – Some years ago, we have investigated the flash photolysis of 2,2′-azobis(isobutyronitrile) (=2,2′-azobis[2-methylpropanenitrile]; AIBN) resulting in a N_2 molecule and a geminate pair (G-pair) of two 2-cyanoprop-2-yl radicals (*Scheme*) [1]. The cleavage occurs from an excited singlet state and, therefore, a considerable fraction of the G-pairs decays rapidly by radical termination to form 'in-cage' recombination and disproportionation products. Those species that escape the geminate cage effect diffuse apart and form F-pairs by subsequent random free-diffusive encounters. There, they terminate when they happen to encounter in a singlet-pair spin state. Most of those encountering in a triplet-pair spin state escape the F-pairs.

The radicals escaping the G- and F-pairs exhibit chemically induced electron polarization (CIDEP), *i.e.*, the populations of their spin states deviate from thermal equilibrium. This phenomenon is due to the radical-pair mechanism (RPM) and arises during diffusive re-encounter sequences of the spin-correlated G- and F-pairs *via* mixing and splitting of the singlet- and triplet-pair spin states by the hyperfine and exchange interaction [2–4]. The magnitudes of the G- and F-pair polarizations, P_G and P_F, respec-

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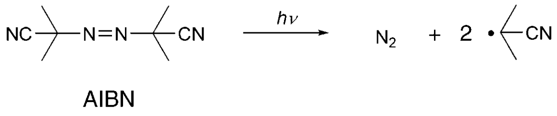
Scheme



tively, are determined by several microscopic quantities. However, the ratio of both polarizations, $|P_F/P_G|$, has been found [1] to have a sensitive dependence on essentially only the initial spatial separation r_i of the two radicals in the spin-correlated pairs, because the G- and F-pairs, after photolysis of AIBN, are both composed of two 2-cyanoprop-2-yl radicals and, therefore, all details concerning the diffusion and the distance dependence of the exchange interaction are the same for both pairs. With respect to the RPM, the essential difference between both pairs is only the initial spatial distance in which the radicals start their diffusive trajectories of the separation and re-encounter process, along which the CIDEP is generated.

For the F-pairs, the initial distance, where the CIDEP starts to develop, is the reaction distance, which can be estimated from radical radii. The initial radical separation r_i in the G-pairs is not well-known. After photo-dissociation of a molecule in solution, there seems to be a fairly short (femto- to picosecond) primary separation stage of the fragments, accompanied by fast vibrational and translational relaxation [5][6]. After dissipation of the initial energy, those radicals that have escaped fast recombination during the primary separation stage will have a certain distribution of initial distances r_i, from where the diffusive separation and re-encounter sequences start.

An average of the initial r_i distribution may be estimated from *Langevin* models. It determines not only the polarization ratio $|P_F/P_G|$, but plays an important role also in modeling the cage effect, *i.e.*, the in-cage recombination of the G-pair radicals. As mentioned above, this cage-effect is composed of a 'primary' and a 'secondary' one [7]. The primary effect occurs on the femtosecond-to-picosecond time scale during separation of the fragments and dissipation of the excess energy. It has no direct connection with r_i. The secondary one, however, is determined by the probability for diffusive return of the radicals from r_i to the reaction distance. Thus, any meaningful model for the viscosity dependence of r_i must be able to reproduce the viscosity dependence of both the total cage effect and the ratio of spin polarizations $|P_F/P_G|$.

In former work [1], we have reported on quantitative, time-resolved electron-paramagnetic-resonance (EPR) measurements of the spin polarizations, which are generated in G- and F-pairs after photolysis of AIBN in solvents of different viscosity, and we have also determined the geminate cage effect P_C, *i.e.*, the probability for in-cage radical termination. We found that common *Langevin* models for r_i are unable to describe consistently the viscosity dependence of both the cage effect P_C and the spin-polarization ratio $|P_F/P_G|$.

Here, we consider that this failure might result from the strong dipole–dipole interaction between the polar 2-cyanoprop-2-yl radicals. First, we will compile briefly the data obtained for the AIBN photolysis. We will then show that the *Langevin* models work properly for the photolysis of azocumene into N_2 and two rather nonpolar cumyl radicals, and will finally propose a primary caging model for polar radicals that gives a consistent description of the behavior of the polar 2-cyanoprop-2-yl radicals.

Results and Discussion. – In our previous investigation [1] of 2-cyanoprop-2-yl radicals formed by photolysis of AIBN in liquid solutions of different viscosities, we have determined the probability P_C for geminate in-cage radical termination, as well as the spin polarizations P_F and P_G of the radicals escaping the F- and G-pairs. The absolute value of the ratio of the polarizations is denoted as $R_e = |P_F/P_G|$. The terms P_C as well as R_e were found to depend on the viscosity η of the solution, reflecting a certain viscosity dependence of the initial separation r_i of the two 2-cyanoprop-2-yl radicals in the geminate pair. For comparison of the experimental finding with predictions of common *Langevin* models, we found it convenient to use dimensionless variables and to describe possible dependencies of r_i on η with the combined expression:

$$\Delta x(q) \equiv (r_i - d)/d = \delta + \lambda_1/\sqrt{q} + \lambda_2/q \tag{1}$$

In *Eqn. 1*, d is the distance of closest approach of both radicals, δ, λ_1, and λ_2 are adjustable parameters, and q is a dimensionless viscosity defined as $q \equiv Ad^2/D \sim 1/D \sim \eta$, A being the hyperfine splitting and D the diffusion coefficient[2]). The three terms on the right-hand side of *Eqn. 1* take into account three possible scenarios that might determine r_i. The last term considers the most-popular model of primary separation given by *Noyes* [8], assuming that, after formation, the radicals move apart from each other because of an initial translational energy that, at r_i, is used up by the work against friction. The second term accounts for a possible diffusion-like primary separation, where the mobility of the radicals is determined by a local heating effect due to excess energy, which would result in a dependence $\Delta x(q) \sim q^{-1/2}$. Finally, the first term on the right hand side considers the loss of N_2 in the dissociation process. When N_2 acts as some kind of spacer between the radicals and governs the initial distance, one would expect r_i to be essentially independent of the viscosity, *i.e.*, $\Delta x(q) = \delta = \text{constant}$ (for details, see [1]).

Fig. 1 shows the experimental data for R_e and P_C, together with the theoretical dependencies $R_e(q)$ and $P_C(q)$ for D-dependent initial distances r_i calculated from *Eqn. 1* for $\delta = 0$, $\lambda_2 = 0$ (the dependence $\Delta x \sim \sqrt{D} \sim 1/\sqrt{q}$), and for $\delta = 0$, $\lambda_1 = 0$ (the dependence $\Delta x \sim D \sim 1/q$), respectively. Obviously, the dependence $\Delta x \sim D$ as well as $\Delta x \sim \sqrt{D}$ enables one to get a rather good agreement between theory and experiment for $P_C(q)$. However, the behavior of the CIDEP dependence $R_e(q)$ is predicted in complete contradiction with the experimental one.

The same functions $R_e(q)$ and $P_C(q)$, but for r_i independent of q ($\lambda_1 = \lambda_2 = 0$), are shown in *Fig. 2*. They were calculated for different values of a parameter L_{SS}, which characterizes the effective reaction- and spin-exchange radii [1]. It is seen that, for reasonable values of r_i, the experimentally obtained dependence of the ratio of the F- and G-pair CIDEP, *i.e.*, $R_e(q)$, can be reproduced quite well. At the same time, the agreement for the cage effect $P_C(q)$ is much worse: the theoretical dependence on q is too

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[2]) The symbol '~' means 'proportional to'.

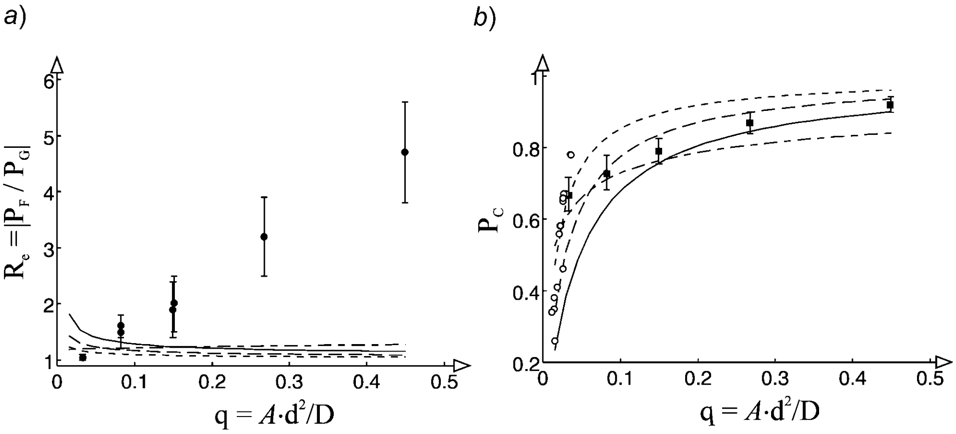

Fig. 1. *Comparison of the experimental* q*-dependencies of* a) *the polarization ratio* ($R_e(q)$) *and* b) *the cage effect* ($P_C(q)$) *with theoretical predictions.* The calculated values were obtained for the free-diffusion model using $\Delta x(q) = \Delta r/d = 0.025/q$ (– –); $\Delta x(q) = 0.015/q$ (---); $\Delta x(q) = 0.04/q$ (——); and $\Delta x(q) = 0.10/\sqrt{q}$ (– – –).

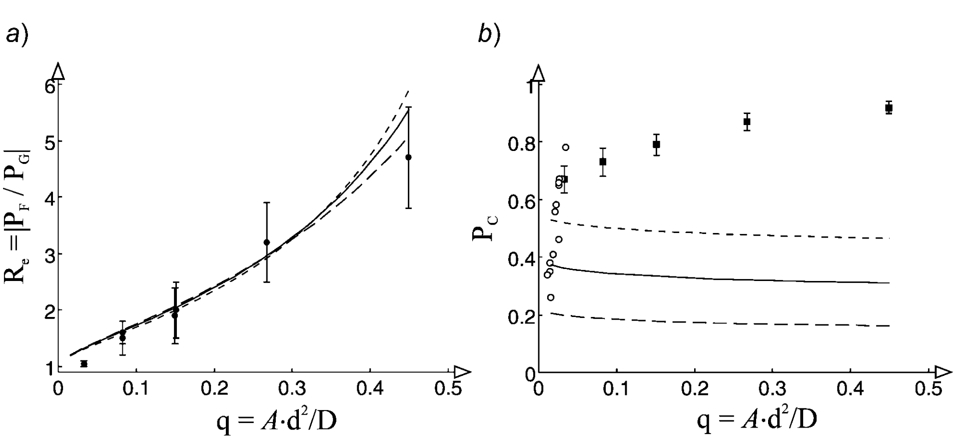

Fig. 2. *Comparison of the experimental* q*-dependencies of* a) *the polarization ratio* ($R_e(q)$) *and* b) *the cage effect* ($P_C(q)$) *with theoretical predictions, but for* $\Delta x(q)$ *independent of* q. The values were obtained using $\Delta x = 1.2$, $L_{SS}/d = 0.5$ (– –); $\Delta x = 1$, $L_{SS}/d = 0.8$ (——); and $\Delta x = 0.8$, $L_{SS}/d = 1$ (---).

weak, is decreasing with q, and is of lower absolute value as compared to the experimental one.

Of course, one can find compromises by setting all three parameters in *Eqn. 1* unequal to zero, but any pronounced decrease of r_i with increasing viscosity, as is needed to describe the cage effect, weakens the change of R_e towards unity. Unambiguously, for the 2-cyanoprop-2-yl radical pairs, the classic *Langevin* models for the initial separation r_i are not capable of simultaneously describing the viscosity dependence of the cage effect and the CIDEP.

This finding is in contrast to results obtained in an investigation of cumyl radicals formed by photolysis of *trans*-azocumene (=(*E*)-bis[2-(1-methylethyl)phenyl]diazene)

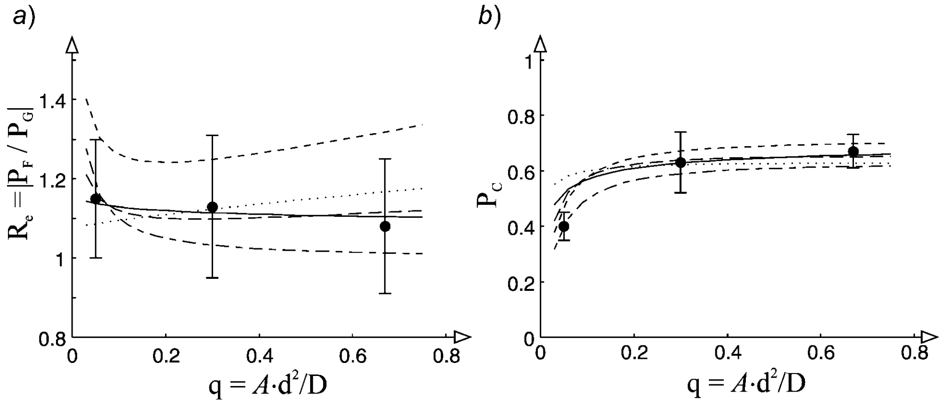

Fig. 3. *Experimental and theoretical results for the photolysis of* trans-*azocumene.* a) Comparison of calculated *vs.* theoretical $R_e(q)$ values (*a*) and $P_C(q)$ values (*b*). The theoretical values were calculated within the classic *Langevin* models for $\Delta x(q) = 0.03/q$, $L_{SS}/d = 0.7$ (– – –); $\Delta x = 0.15 + 0.03/$, $L_{SS}/d = 0.9$ (---); $\Delta x = 0.1 + 0.05/\sqrt{q}$, $L_{SS}/d = 0.8$ (· · ·); $\Delta x = 0.1 + 0.02/q$, $L_{SS}/d = 0.8$ (– – –); and $\Delta x = 0.1/\sqrt{q}$, $L_{SS}/d = 0.8$ (——).

in solvents of different viscosities [9]. The experimental data and theoretical predictions for this system are depicted in *Fig. 3*. It shows three experimental values and the theoretical functions $R_e(q)$ and $P_C(q)$ for initial distances r_i estimated from *Eqn. 1* using different parameters δ, λ_1, and λ_2. The effective reaction radius L_{SS} was also varied. It is seen that both experimentally obtained dependencies, the polarization ratio $R_e(q)$, and the cage effect $P_C(q)$, can be reproduced quite well for the cumyl radicals. The parameters $0 \leq \delta \leq 0.2$ and $0.7d \leq L_{SS} \leq d$, required for accurate description of the experimental results, are quite reasonable. The q-independent initial separation $\delta = (r_i - d)/d$ does not exceed the maximum value $\delta \approx 0.5$, which can be estimated from $d = 6.2$ Å for cumyl and $d_{N_2} \approx 3.4$ Å for nitrogen [10]. Further, the effective radius of recombination in the singlet state, $L_{SS} \approx d$, shows that the self-termination of cumyl radicals is close to diffusion control.

Unfortunately, the quality of the experimental data does not allow any differentiation of the three separation models for r_i contained in *Eqn. 1*, but they certainly demonstrate that the classic *Langevin* models are able to reproduce semiquantitatively the observed viscosity dependence of the cage effect as well as the CIDEP for cumyl radical pairs generated by photolysis of *trans*-azocumene.

The reason for this discrepancy between the azocumene and AIBN photolysis system is probably due to different interactions between the two rather nonpolar cumyl and the two polar 2-cyanoprop-2-yl radicals. It seems that a consistent simultaneous theoretical modeling of both $R_e(q)$ and $P_C(q)$ for the AIBN system requires a consideration of the dipole–dipole interaction between the 2-cyanoprop-2-yl radicals during the geminate separation process. A suitable primary caging model for polar radicals is outlined in the following section.

Primary Caging Model for Polar Radicals. – The radical $Me_2\dot{C}CN$, for convenience denoted hereafter as R–CN, has a planar structure at the central C-atom and a strong dipole moment ($\mu_e \approx 4$ D) [11] concentrated on the CN group of length $l \approx 1.16$ Å. This large dipole moment results from a rather strong charge separation in the CN group, which leads to some peculiarities of the interaction between two of these radicals. The characteristic features of the inter-radical interaction between two R−CN radicals is conveniently analyzed in the simple model of two spheres of radius $R = 2.5$ Å, with dipole moment $\mu_e^a = \mu_e^b = 4$ D, located at the sphere surfaces (*Fig. 4*). The analysis shows that, in the multidimensional space of relative orientations and distances between the radicals, there are very wide attractive and repulsive regions. It is of importance for the further discussion that, at contact distance d, the statistical weight of orientations corresponding to strong attraction between the radicals is quite large, accounting for *ca.* 10% of the complete orientational volume of the system. For example, for one of the dipoles oriented to the other, the interaction is attractive for almost all orientations of the second dipole, and the interaction at contact distance is stronger than 5 kT. As the second dipole turns to the first one, the attraction increases, and for some orientations it exceeds 20 kT. This means that in a quite wide region of the coordinate space of the radical pair there exists a rather deep well of the inter-radical dipole−dipole interaction potential, which can strongly affect the relative motion of the species (see below) [12][13].

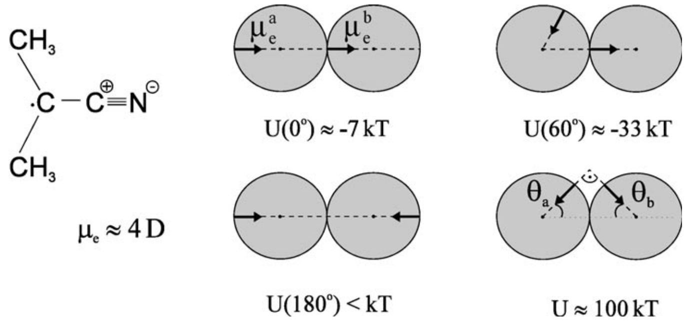

Fig. 4. *Schematic representation of the polar orientations* (in terms of angles θ) *of the electric dipole moments* (μ) *of a* $Me_2\dot{C}$*–CN radical pair*

The strong dipole−dipole interaction already shows up in the reactivity of the R−CN radical pairs when compared to those composed of two $Me_3\dot{C}$ radicals. The termination of two R−CN radicals yields *ca.* 95% of combination products: the ketene-imine (KI) $Me_2C{=}C{=}N{-}C(Me_2)CN$[3]) and the tetramethylbutanedinitrile $NC{-}C(Me)_2$-$C(Me)_2CN$, also known as 'tetramethylsuccinodinitrile' (TMSN). Here, disproportionation is much less efficient (*ca.* 5%) [9]. In contrast to this, the termination of two *tert*-butyl radicals ($Me_3\dot{C}$) proceeds mainly *via* the disproportionation channel (*ca.* 85%) [14].

The significant difference of the branching ratios of termination for these two radical pairs can be easily rationalized by taking into account the strong electrostatic dipole−dipole interaction between the radicals R−CN. Indeed, simple inspection shows that the most-attractive orientations, $\theta_a < \pi/3$, $\theta_b \approx 0$ (*Fig. 4*), are just favorable

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[3]) Systematic name: 2-methyl-2-[(2-methylprop-1-en-1-ylidene)amino]propanenitrile.

for the reaction yielding KI. The orientations favorable for the direct recombination (TMSN) are less attractive, but are still located in the region of attractive dipole–dipole interaction. In the absence of electrostatic interactions, *i.e.*, for neutral radical pairs like those of $Me_3\dot{C}$, the disproportionation reaction dominates because of a much larger statistical weight of favorable orientations. However, a significant electrostatic dipole–dipole interaction does not only influence the branching ratio of reactions in the bimolecular radical termination, but also, because of the corresponding potential well at short distance, is expected to change the efficiency of separation of radicals at early times of evolution and short distances.

In liquids, the combined effect of such attractive inter-radical interactions, as well as interactions of the radicals with surrounding molecules, is usually described by a mean-force potential (MFP) U_r involving the pair-distribution function $g(r)$ [15–17].

$$U(r) = -kT\ln[g(r)] \tag{2}$$

The typical distance dependence of $U(r)$ is schematically shown in *Fig. 5*. The important characteristic feature of the MFP is the presence of a well at distances r of order of the distance of closest approach d (approximately the distance of the first coordination shell). The well depth depends on the strength of both radical–radical and radical–solvent interactions. However, an especially deep attraction well at $r \approx d$ is expected due to the strong electrostatic interaction between the R–CN radicals. Usually, the MFP also possesses a broader and more-shallow well at distance $r \approx 2d$ corresponding to the second coordination shell. Attraction at short distance ($r \approx d$) leads to caging, *i.e.*, a relatively long-lived intermediate state of the radical pair in the well.

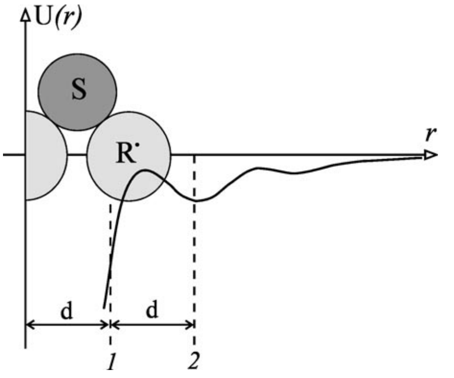

Fig. 5. *Mean force potential* (U) *of interaction between two radicals as a function of distance* (r)

In the presence of the well, the following scenario of the primary radical separation seems to be quite realistic: at the initial short time, just after the reaction, the radical pair is created at contact distance $r = d$ with a strong excess of energy. The initial stage after dissociation of the excited precursor molecule is the stage of VRT relaxation (equilibration) of radicals within the well at $r \approx d$, and thermal relaxation of the surrounding molecules in the first coordination shell. This process can be thought as a fast cooling of radical pairs in the cage of closest solvent molecules. During this initial stage, some radical pairs dissociate to the area of the second, less-attractive well of the second coordination shell at $r \approx 2d$. The spatial distribution of radical pairs escaping from the deep well at $r \approx d$ after this fast stage can be considered as the initial condition for the second magnetic-field-dependent stage. It is important to note that radical pairs in the well at $r \approx d$ can hardly contribute to the CIDEP because of fast spin relaxation induced by the electron-spin exchange and dipole–dipole interactions. However, these interactions are still relatively weak and, as far as the electronic and vibrational properties are concerned, the radicals of the pairs within this well can be considered as separate. In other words, radical pairs within the well at $r \approx d$ are assumed to strongly contribute to the pair-recombination probability, but make no contribution to the CIDEP. This model, which takes into account the effect of the potential well in the primary separation of the species, will be called hereafter 'primary caging model' (PCM).

Semiquantitatively, the fast first stage of separation in the PCM is described by simple kinetics equations (*Eqn. 3*) for the populations n_1 and n_2 of the first deep well (first coordination shell; $r \approx d$) and the second shallow well ($r \approx 2d$), respectively:

$$d(n_1)/dt = -w_{21} \cdot n_1 + w_{12} \cdot n_2 \tag{3a}$$

$$d(n_2)/dt = w_{21} \cdot n_1 - w_{12} \cdot n_2 \tag{3b}$$

Here, w_{12} and w_{21} are the rates of transitions from the second to the first well and *vice versa*, respectively, *i.e.*, the forward ($2 \rightarrow 1$) and backward ($1 \rightarrow 2$) processes. The initial condition $n_1(0) = 1$ and $n_2(0) = 0$ implies that the radical pair is created in the first well at $r \approx d$. During the equilibration (cooling) time τ_e, the radical pair jumps to state 2 (second well) with the probability:

$$n_2(\tau_e) = 1 - n_1(\tau_e) = (w_{21}/w) \cdot (1 - e^{-w \cdot \tau_e}) = n_2^{\infty} \cdot (1 - e^{-w \cdot \tau_e}) \tag{4}$$

in which $w = w_{12} + w_{21}$ and $n_2^{\infty} = w_{21}/w$. Both w_{12} and w_{21} are expected to be inversely proportional to the solvent viscosity η, in accordance with *Kramers*' prediction for overdamped regimes [18]. In this case, n_2^{∞} is independent of η and $w \sim \eta^{-1}$. The equilibration time τ_e is typically determined by fast VV and VT processes in liquids, and is practically independent of the viscosity [5][19]. In such a case, for short equilibration times τ_e, when $w \cdot \tau_e < 1$, *Eqn. 4* yields the simple viscosity dependence $n_2(\tau_e) \approx w_{21} \cdot \tau_e \sim \eta^{-1}$.

After equilibration, no transitions from the first well to the second are assumed to occur because of the large depth of the well at $r \approx d$. This means that the CIDEP is determined only by the radical pairs that have escaped from the first well and appeared in the region of the well at $r \approx 2d$. In this model, the recombination of radical pairs is treated as a capture of radicals into the well at $r \approx d$ during their relative diffusion. When the recombination probability of state-2 diffusing radical pairs is P_r, then the total recombination probability P_C (which can be observed experimentally and associated with the 'cage effect') is given by *Eqn. 5*:

$$P_C = n_1 + n_2 \cdot P_r = 1 - n_2 \cdot (1 - P_r) = 1 - n_2^{\infty} \cdot (1 - e^{-w \cdot \tau_e}) \cdot (1 - P_r). \tag{5}$$

The value of P_r as well as the magnitude of the CIDEP depend on the distribution of the radical pairs over the initial distance r_i, *i.e.*, the distance distribution $\rho_2(r_i)$ in state 2.

When, as before for the *Langevin* models, the spread of distances in this state is neglected, then this distribution is given by *Eqn. 6*:

$$\rho_2(r_i) = \frac{n_2}{4 \cdot \pi \cdot r_i^2} \cdot \delta(r - r_i). \tag{6}$$

The initial distance r_i is considered as an adjustable parameter of the model. Its value is restricted, however, by the condition $r_i \approx 2d$.

It is instructive to analyze the possible relation of the PCM to the *Langevin* models mentioned above. Interestingly, despite of the different basic physical assumptions of the PCM and the model by *Noyes* [8], both of them predict a similar dependence $d\Delta x = \Delta r \sim \eta^{-1}$ in a wide region of parameters. In the PCM model, *Eqn. 3* ($\Delta r \sim \eta^{-1}$) is obtained in the limit $w \cdot \tau_e < 1$, taking into account that $\Delta r = n_2 \cdot (r_2 - d) \sim w_{21} \cdot \tau_e \cdot (r_2 - d) \sim \eta^{-1}$, where $r_2 \approx 2\mathrm{d}$ is the average distance between radicals in the second shell, and that r_2 and τ_e are basically independent of η.

In fact, the discrepancy between theory and experiment, which arises when r_i of the R–CN radicals is estimated from the *Langevin* models, can easily be resolved in the PCM considered above. It is worth reminding that, unlike the diffusion models, in the PCM there are two contributions to the cage effect (recombination probability): one coming from the first stage of recombination in the potential well, which is located in the region of the first coordination shell ($r \approx d$), the other stemming from the second stage of free diffusion outside the well starting from the distance $r_i \approx 2d$ of order of the radius of the second coordination shell, *i.e.*, independent of $D \sim 1/q$. At the same time, the CIDEP is determined only by the second stage of free diffusion, *i.e.*, is calculated for the initial distance $r_i \approx 2d$ independent of q. In other words, the PCM predicts the same CIDEP as the diffusion model, but with r_i (or Δr) independent of q. Note that just in the case of r_i being independent of q the diffusion model reproduces quite accurately the experimental behavior of the CIDEP dependence on q.

As already shown, the diffusion model with constant r_i does not reproduce the experimental behavior of $P_C(q)$ (cage effect; *Fig. 2*). The PCM rationalizes the higher value of the experimental $P_C(q)$ by the above-mentioned contribution of the first stage of separation. *Eqn. 5* provides the expression for $P_C(q)$ in the PCM in terms of the initial populations n_1 and n_2 of state 1 (within the well) and of state 2 (outside the well), and the calculated probability $P_r(q)$ of recombination from state 2, *i.e.*, the recombination probability calculated in the diffusion model for $r_i \approx 2d$. The dependence of the so-obtained $P_C(q)$ on the diffusion coefficient $D \sim 1/q$ is determined by the D-dependence of $P_r(q)$ and the populations n_1 and n_2 given by *Eqn. 4* (in this expression, the rate $w \sim D$ and the equilibration time τ_e are independent of D).

Fig. 6 shows a comparison between the experimental and theoretical function $P_C(q)$. In calculation of the theoretical values of $P_C(q)$, the parameter β in the dependence $w \cdot \tau_e = \beta/q$ and the parameter $n_2^\infty = n_2(\tau_e \gg w^{-1}) = w_{21}/w$ are considered as adjustable. It is seen that the PCM improves significantly the agreement between theory and experiment. The rather large value of $n_2^\infty \approx 1$, required for an accurate description of the experiment, is quite reasonable because it corresponds to the seemingly obvious statement that, at low viscosities during the primary separation, the radical pairs escape from the well at $r \approx \mathrm{d}$ with a probability close to unity.

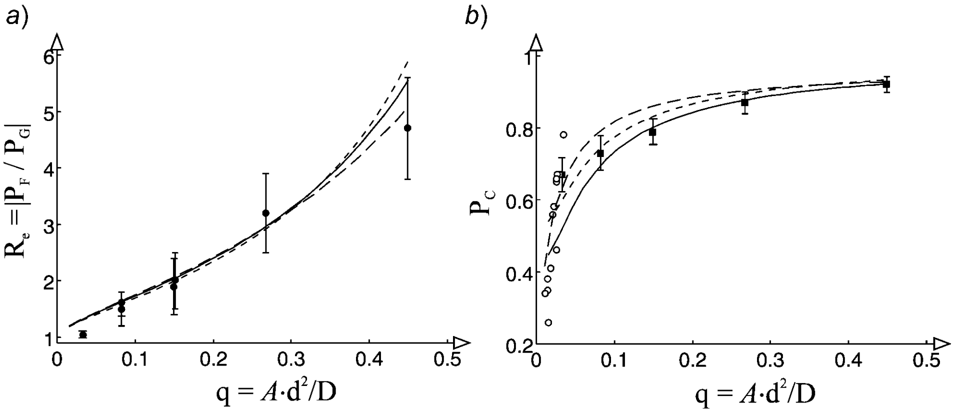

Fig. 6. *Same as* Fig. 2*, but in the PCM model.* The cage effect $P_C(q)$ was calculated by *Eqn. 5*. For the first stage, the following parameters were used: $n_2^\infty = w_{21}/w = 0.9$, $w \cdot \tau_e = 0.04/q$ (– –); $n_2^\infty = 0.9$, $w \cdot \tau_e = 0.05/q$ (——); and $n_2^\infty = 1$, $w \cdot \tau_e = 0.06/q$ (- - -). For the second, free-diffusion stage, the corresponding parameters of *Fig. 2* were taken.

It is also important to emphasize that fitting requires values of the parameter β, which corresponds to values $w \cdot \tau_e \approx 1$ for the experimentally investigated solvents for which D is 10^{-5} to 10^{-4} cm^2 s^{-1}. This provides the opportunity of estimating the escape rate $w_{21} \approx w \approx 1/\tau_e$ for typical values of τ_e in the order of the vibrational relaxation time in liquids ($w \approx 10^{12} - 10^{13}$ s^{-1}).

In summary, the above comparison shows that the PCM allows one to interpret semiquantitatively the available experimental results on both the viscosity dependence of the cage effect and the CIDEP for pairs of strongly interacting 2-cyanoprop-2-yl radicals, and to obtain important information on the mechanism and characteristic parameters of the primary separation stage for these radicals. It is important to note in addition that the PCM offers a reasonable explanation of the qualitative difference of the experimentally observed viscosity dependence of the cage effect for the radical pair 2 $Me_2\dot{C}{-}CN$ and the related process leading to a pair of nonpolar $Me_2\dot{C}Ph$ radicals upon azocumene decomposition.

The authors are grateful to the *Swiss National Foundation for Scientific Research* for financial support of this work. *A. I. S.* acknowledges a grant from the *Russian Foundation for Fundamental Research*.

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Received August 15, 2006