obtained from the PPP method. The calculated values are in good agreement with those derived from MCD and uv spectra.[15,16] Our calculations suggest that the magnetic moments in the $^1E_{1u}$ and $^1E'$ states of benzene derivatives are increased by the substitutions of electron-donating functions and are quenched by the effects of electron-accepting substituents, which is consistent with the experimental data. It may be concluded that the PPP method is available for the calculations of the magnetic moments of aromatic molecules. An unsatisfactory result for 1,3,5-tricyanobenzene may arise from the choice of the semiempirical parameters of the PPP method and the effective nuclear charges, or the scheme determining the wave functions in the excited electronic states.

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Diffusion Model Analysis of Cage Reactions of Chiral Radical Pairs

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Abstract: The diffusion radical pair model of Noyes is used in the analysis of data on the extent of racemization accompanying formation of cage coupling products in decompositions of radical pair precursors RMX, where R is the chiral group 1-phenylethyl, M is a small molecule extruded in the decomposition, and X is another group. It is found that the fraction s of retention of configuration (vs. racemization) in the coupling product is $e^{-2(a/\tau_r)^{1/2}}$, where a is a parameter dependent on the reactivity and diffusion characteristics of the radicals and τ_r is the rotational relaxation time of R·. There is excellent agreement between τ_r estimated on this basis from experimental data and τ_r estimated from dielectric relaxation experiments on ethylbenzene, a model for R·. Experiments involving decompositions of RMR can, in principle, serve to distinguish the diffusion model from a much simpler model in which radical pair recombination and diffusive separation are taken to be first-order processes. Unfortunately, when $D\tau_r$ is in its usual range (D = relative diffusion coefficient of the radicals), the method is not likely to succeed because of insufficient differences between the predictions of the two models. The treatment of this problem is closely related to that of the encroachment of scavengers on secondary geminate recombination, for which an equation, obtained by Noyes in the form of a truncated series, is given.

Reactive free radicals generated as pairs in solution may react with one another before diffusing apart or reacting with scavengers which may be present. Relevant to such "cage reactions"[2,3] or "geminate recombinations"[4] there exists a substantial body of theory and experiment.[2]

Data have been obtained recently for several cases in which the cage reactions compete with the racemization of initially chiral radical pairs (eq 1).[5-7] In RMX, R is a chiral

$$\begin{tikzcd}
 & & \mathrm{R\cdot + X\cdot}\ \text{(scavenged by added trap)} & \\
\mathrm{RMX} \arrow[r] & (\mathrm{R\cdot X\cdot}) \arrow[ur] \arrow[rr, shift left, "k_r"] \arrow[d] & & (\mathrm{R'\cdot X\cdot}) \arrow[ul] \arrow[ll, shift left, "k_r"] \arrow[d] \\
 & \mathrm{P} & & \mathrm{P'}
\end{tikzcd} \qquad (1)$$

group (1-phenylethyl in the cases so far studied), M is a small molecule extruded in the thermal decomposition (e.g., nitrogen or carbon dioxide), and X is another group (in one case studied, X = R). (R′·X·) is a radical pair in which the radical R· has rotated to expose to X· the face opposite that through which it was originally bound; (R·X·) and (R′·X·) are enantiomeric radical pairs which collapse to give products P and P′, respectively. The rotation of R· is a first-order process governed by the rate constant k_r or the relaxation time $\tau_r = 1/2k_r$. Radical pairs which suffer separation by diffusion are scavenged by a radical trap which is present, so that P and P′ are formed only in cage reactions. Experimentally, the cage yield b and the fraction s of retention of configuration (the remainder being racemization) in the combination products RX are determined. In Table I are collected experimental values of b and s.

The data were treated originally in terms of a "first-order" model in which radical pair reaction and diffusive separation are governed by first-order rate constants k_c (cage reaction) and k_d (diffusive separation).[5-7] However,

Table I. Experimental Data on Cage Reactions of Chiral Radical Pairs

Example	Thermal source	Solvent	Temp[d]	b[e]	s[f]
1	**1**[a]	Benzene	110	0.28	0.103
2	**1**	Cyclohexane	115	0.32	0.109
3	**1**	Chlorobenzene	108	0.33	0.130
4	**1**	Butanethiol	110	0.18	0.173
5	**2**[b]	Cumene	60.1	0.42	0.208
6	**3**[c]	Benzene	105	0.32	0.107

[a] *S*-(−)-1,1′-Diphenyl-1-methylazomethane; ref 5. [b] *S*-(+)-*tert*-Butyl 2-phenylperpropionate; ref 6. [c] *(S,S)*-(−)-Azobis-α-phenylethane; ref 7. [d] Temperature in °C. [e] Cage reaction efficiency. [f] Fraction of retention, the remainder being racemization, in the cage recombination products. In example 6, this is computed for all R groups in all three combination products: s = (mol RR − mol R′R′)/(mol RR + mol RR′ + mol R′R′).

Table II. Analyses of Data from Cage Reactions of Chiral Radical Pairs in Terms of the First-Order Model

Example[a]	y[b]	$10^{-11}D$[c] (est)	$10^{-11}k_d$[d] (est)	$10^{11}\tau_r$[e] (est)	$10^{11}\tau_r$ (20°)[f] (est)
1	8.71	5.6	0.50	0.17	0.37
2	8.17	5.8	0.52	0.17	0.37
3	6.69	5.5	0.49	0.20	0.45
4	4.78	5.6	0.50	0.34	0.77
5	3.81	3.4	0.30	0.50	0.76
6	8.35	5.4	0.48	0.17	0.37

[a] See Table I for experimental data. [b] $y = 1/(k_c + k_d)\tau_r$. [c] Relative diffusion coefficient (Å²/sec) at the temperature of the experiment, estimated as described in text. [d] Rate constant (sec⁻¹) for diffusive separation of radical pairs, estimated as described in text. [e] Rotational relaxation time (sec⁻¹) of 1-phenylethyl radicals under experimental conditions, estimated from experimental data as described in text. [f] Rotational relaxation time of 1-phenylethyl radicals at 20°, estimated as described in text.

if these cage reactions are "secondary recombinations",[4] i.e., recombinations of radicals which do not occupy adjacent positions in solution initially, then radical pair reactivity should be governed by appropriate equations of diffusion.[4,8] Noyes' equation (eq 2) is taken to define the "diffusion model".

$$h(t) = b\sqrt{\frac{a}{\pi}}\,e^{-a/t}t^{-3/2} \tag{2}$$

Here, $h(t)\,dt$ is the probability that a radical pair will suffer secondary recombination between times t and $t + dt$, b (Noyes' β')[4,8] is the cage efficiency, as before, and a is a constant depending on diffusion and reactivity parameters.[9] Equation 2 does not describe a first-order process or the competition of first-order processes. To the extent that it is correct, the first-order model is incorrect.

Where primary recombination is possible, i.e., where the radicals occupy adjacent positions in solution initially, there may be an immediate contribution to cage reaction that is not governed by eq 2. However, where there is initially an intervening molecule M, as in the cases treated here, this consideration does not apply. Although there are several instances in which the encroachment of scavenging on the cage effect follows a law predicted from eq 2 (linear dependence on $[S]^{1/2}$, where S = scavenger),[4] there is also an example in which it is apparently not followed.[10] CIDNP data, however, seem to support the diffusion model.[11]

Here, the data on cage reactions of chiral radical pairs are analyzed in terms of the diffusion model. For comparison, analyses in terms of the first-order model are also presented. It is shown that data from certain chiral radical pair reactions can, in principle, distinguish between the first-order and diffusion models, but that, in practice, appropriate data may be difficult or impossible to obtain. Finally, the relationship between the equations describing chiral radical pairs and those describing the scavenging of secondary recombination is pointed out.

According to the first-order model,

$$b = k_c/(k_c + k_d) \tag{3}$$

and

$$s = y/(1 + y) \tag{4}$$

where $y = 1/(k_c + k_d)\tau_r$. These equations result from straightforward algebra which is not given here; they are equivalent to the relationships used by Kopecky[5] and Greene.[6,7]

According to the diffusion model, the probabilities A and A' of formation of products P and P′ are given by eq 5,

$$A = \int_0^\infty h(t)p(t)\,dt \tag{5a}$$

$$A' = \int_0^\infty h(t)p'(t)\,dt \tag{5b}$$

where $p(t)$ is the probability that a radical pair, generated as (R·X·) at time zero, is (R·X·) at time t (if it has not reacted), and $p'(t)$ is the corresponding probability that it is (R′·X·). $p(t)$ and $p'(t)$ are given by eq 6 and the integrated forms of A and A' by eq 7. If combination products are a fraction f of both P and P', then s is given by eq 8.

$$p(t) = 0.5(1 + e^{-t/\tau_r}) \tag{6a}$$

$$p'(t) = 0.5(1 - e^{-t/\tau_r}) \tag{6b}$$

$$A = (b/2)(1 + e^{-2(a/\tau_r)^{1/2}}) \qquad (7a)^{12}$$

$$A' = (b/2)(1 - e^{-2(a/\tau_r)^{1/2}}) \tag{7b}$$

$$s = (fA - fA')/(fA + fA') = e^{-2(a/\tau_r)^{1/2}} \tag{8}$$

From the experimentally derived parameters y and a/τ_r, τ_r can be estimated in a variety of ways. Two of these are presented here, one for the first-order model and one for the diffusion model.

Let two noninteracting spheres be defined as a "pair" if they are within a distance $\rho + \Delta$ of one another, where ρ is the collision diameter. The "dissociation constant" K_d for such pairs in dilute solution is given by eq 9,[13] where N is the Avogadro number.

$$K_d = (4\pi N\rho^2\Delta)^{-1} \tag{9}$$

The rate constant for formation of these pairs is the conventional bimolecular encounter rate constant k_e (eq 10),[14] where D is the relative diffusion coefficient (the sum of the individual diffusion coefficients of the spheres).

$$k_e = 4\pi N(\rho + \Delta)D \tag{10}$$

Since $K_d = k_d/k_e$,

$$k_d = D(\rho + \Delta)/\rho^2\Delta \tag{11}$$

Let Δ be the size of N_2 (4.1 Å; N_2 bond length plus two N van der Waals radii), and let ρ = 5 Å. To estimate D the properties of the benzyl radical in cyclohexane are assumed for the radicals and solvents of Table I. The diffusion coefficient of a benzyl radical in cyclohexane at 25° is 1.1×10^{-5} cm²/sec.[15] Since the formal activation energy for diffusion is 2–3 kcal/mol for ordinary solutes in most fluid solvents, 2.5 kcal/mol is adopted to correct D to the temperatures of the experiments. Equation 11 then gives k_d, and $\tau_r = (1 - b)/k_d y$. A typical activation energy for molecular rotation seems to be 2.0 kcal/mol; this value applies to fluorenone in benzene.[16] Using it, τ_r is corrected to 20°, where rotational relaxation times of several benzene derivatives have been determined.[17] The results of these calculations are given in Table II.

Equations given by Noyes,[8] in which he identifies expressions from his particle-pair development with equivalent

Table III. Analyses of Data from Cage Reactions of Chiral Radical Pairs in Terms of the Diffusion Model

Example[a]	a/τ_r	$10^{11}a$ (est)[b]	$10^{11}\tau_r$[c] (est)	$10^{11}\tau_r$ (20°)[d] (est)
1	1.295	0.58	0.45	1.0
2	1.225	0.50	0.41	0.9
3	1.037	0.51	0.49	1.1
4	0.771	0.75	0.97	2.2
5	0.616	0.62	1.00	1.5
6	1.249	0.54	0.43	0.9

[a] See Table I for experimental data. [b] In sec, estimated as described in text. [c] Rotational relaxation time of 1-phenylethyl radicals under experimental conditions, estimated as described in text. [d] Rotational relaxation time of 1-phenylethyl radicals at 20°, estimated as described in text.

ones from a development based on the equations of diffusion, can be rearranged to give an expression for a (eq. 12)

$$a = (1 - b)^2\rho^2/4D \tag{12}$$

in terms of b, D, and ρ, the collision diameter for radicals. Estimating D as before, using the reasonable choice of ρ = 5 Å, and correcting τ_r to 20° as before, estimates of a, τ_r, and $\tau_r(20°)$ are obtained. The results are in Table III.

Perhaps the best model for the 1-phenylethyl radical, for which data are available, is ethylbenzene. In benzene at 20°, τ_r(ethylbenzene) = 1.17×10^{-11} sec.[17] Benzene is the solvent for examples 1 and 6, and the agreement from the diffusion model is excellent ($\tau_r(20°) = 1.0 \times 10^{-11}$ sec and 0.9×10^{-11} sec). To the extent that all the solvents resemble benzene and cyclohexane, the agreement with all the values from the diffusion model, except that for butanethiol, is excellent, and the butanethiol value differs by less than a factor of 2. The values from the first-order model seem too small by a factor of 2-3. This is still sufficiently close that it must be considered within the limits of error of the estimations. Thus, both models give reasonable estimates of τ_r, although the diffusion model may be better.

In principle, the data of Greene, Berwick, and Stowell[7] provide a quantitative test of the two radical pair models and a means of distinguishing them experimentally. The experiment involves the decomposition of an azo compound (**3**) with two identical chiral R groups (1-phenylethyl). The decomposition and cage reactions of **3** can be represented by eq 13. Three sets of cage products, P, P′, and P″, are

$$\begin{tikzcd}
 & & \text{2R}\cdot\text{ (scavenged by trap)} & \\
\text{RMR} \arrow[r] & (\text{R}\cdot\text{R}\cdot) \arrow[ur] \arrow[d] \arrow[r, shift left, "2k_r"] & (\text{R}\cdot\text{R}'\cdot) \arrow[u] \arrow[d] \arrow[l, shift left, "k_r"] \arrow[r, shift left, "k_r"] & (\text{R}'\cdot\text{R}'\cdot) \arrow[ul] \arrow[d] \arrow[l, shift left, "2k_r"] \\
 & \text{P} & \text{P}' & \text{P}''
\end{tikzcd} \qquad (13)$$

formed; the combination products among these are distinguishable, since P and P″ combination products are enantiomers and P′ combination product is meso. In the computations of Table I, information about the distribution of products among P, P′, and P″ was ignored; the only question considered was whether each R group retains its original configuration. In fact, the distribution among P, P′, and P″ is predicted differently by the diffusion and first-order models.

The experimental values are the fraction r of retention of configuration (vs. racemization) in the nonmeso combination products (RR and R′R′) and the ratio n of nonmeso to meso (RR′) combination products. If combination products account for the same fraction f of P, P′, and P″, then

$$r = (A - A'')/(A + A'') \tag{14}$$

and

$$n = (A + A'')/A' \tag{15}$$

Table IV. First-Order and Diffusion Model Predictions of Product Distributions from RMR Decompositions[a]

	First-order model		Diffusion model	
r	y	n	n	a/τ_r
0	∞	1.000	1.000	∞
0.01	99.25	1.005	1.001	7.017
0.03	32.58	1.015	1.005	4.404
0.1	9.243	1.054	1.030	2.222
0.2	4.236	1.118	1.085	1.280
0.3	2.516	1.195	1.164	0.8318
0.4	1.718	1.291	1.274	0.5592
0.5	1.207	1.414	1.431	0.3739
0.6	0.8604	1.581	1.666	0.2406
0.7	0.6055	1.826	2.050	0.1421
0.8	0.4045	2.236	2.799	0.06987
0.85	0.3161	2.582	3.529	0.04244
0.9	0.2312	3.162	4.962	0.02087
0.95	0.1440	4.472	9.176	0.005985
0.98	0.08236	7.071	21.66	0.001067
0.99	0.05556	10.00	42.40	0.0002783
1.00	0	∞	∞	0

[a] R is a chiral group; r is the fraction retention (vs. racemization) in the nonmeso coupling products RR and R′R′; n is the ratio of nonmeso products to meso (RR′). It is assumed that the inherent reactivities of the radicals to form all three coupling products are the same and that the fraction of disproportionation accompanying them is the same.

where A, A', and A'' are the probabilities of formation of P, P′, and P″, respectively.

According to the first-order model,

$$r = (2y + 1)/(y + 1)^2 \tag{16}$$

and

$$n = (y + 1)/y \tag{17}$$

The diffusion model treatment parallels that already given. The probabilities $q(t)$, $q'(t)$, and $q''(t)$ that a radical pair which was (R·R·) at time zero is at time t (R·R·), (R·R′·), and (R′·R′·), respectively, are given by eq 18, 19, and 20,

$$q(t) = [p(t)]^2 = 0.25(1 + 2e^{-t/\tau_r} + e^{-2t/\tau_r}) \tag{18}$$

$$q'(t) = 2p(t)p'(t) = 0.50(1 - e^{-2t/\tau_r}) \tag{19}$$

$$q''(t) = [p'(t)]^2 = 0.25(1 - 2e^{-t/\tau_r} + e^{-2t/\tau_r}) \tag{20}$$

where $p(t)$ and $p'(t)$ are given in eq 10. Then A, A', and A'' are given by eq 21, 22, and 23

$$A = \int_0^\infty h(t)q(t)\mathrm{d}t = \frac{b}{4}(1 + 2z + z^{(2)^{1/2}}) \tag{21}$$

$$A' = \int_0^\infty h(t)q'(t)\mathrm{d}t = \frac{b}{2}(1 - z^{(2)^{1/2}}) \tag{22}$$

$$A'' = \int_0^\infty h(t)q''(t)\mathrm{d}t = \frac{b}{4}(1 - 2z + z^{(2)^{1/2}}) \tag{23}$$

where $z = e^{-2(a/\tau_r)^{1/2}}$, and r and n are given by eq 24 and 25.

$$r = 2z/(1 + z^{(2)^{1/2}}) \tag{24}$$

$$n = (1 + z^{(2)^{1/2}})/(1 - z^{(2)^{1/2}}) \tag{25}$$

Table IV summarizes the predictions based on the two models. Values of r in the range 0.85-0.95 appear to offer the best chances for meaningful experimental discriminations between the models using routine analytical techniques. It is conceivable that analytical techniques of unusually high accuracy and precision could be used successfully with other values of r.

Greene, Berwick, and Stowell[7] obtained r = 0.203 and n = 1.05 with 2-methylnitrosopropane as the scavenger and r = 0.206 and n = 1.11 with thiophenol. These r values are in a region of poor discrimination between the models. Nonetheless, the data can be tested against the predictions. Since the values of r are quite consistent, the predicted values of n are computed from the two models based on the average value of r, 0.2045. From the first-order model, $n = 1.12$; from the diffusion model, $n = 1.09$. Ignoring experimental error, the fit is definitely better for the diffusion model, for which the predicted n lies between the two experimental values. For the first-order model, the predicted n is greater than either experimental value. While these results favor the diffusion model slightly, they carry little weight because the spread in experimental values of n is twice the difference between the calculated values.

To bring the experiment into the range $r = 0.85$ would require a 30-fold increase in $D\tau_r$, other parameters held constant. Any significant increase in D seems out of the question. Thus, one must seek ways to slow rotation without slowing diffusion in a compensating fashion.

However, this kind of test is not restricted to experiments with chiral radical pairs. For any other process which is first-order in radical pairs and which leads to new radical pairs which collapse to distinguishable products, similar equations apply. What is needed is a process with a first-order rate constant in the range 10^9-10^{10} sec^{-1}. Molecular rotation is a little too fast to serve this purpose well.

Finally, we note that the treatment above is closely related to the problem of the scavenging of secondary geminate recombination. If scavenging occurs with a pseudo-first-order rate constant $2k_s[S]$,[4,8] where k_s is the "long-time" second-order rate constant for the reaction between S and R·, then the fraction A of radical pairs which are not scavenged is given by eq 26. This is the exact form corresponding to the approximate (truncated series) integration given earlier by Noyes.[4,8]

$$A = \int_0^\infty h(t)\, e^{-2k_s[S]t}\mathrm{d}t = b e^{-2(2ak_s[S])^{1/2}} \qquad (26)$$

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(12)

$$\int_0^\infty e^{-a/t}e^{-kt}t^{-3/2}\mathrm{d}t = (\pi/a)^{1/2}e^{-2(ak)^{1/2}}$$

The substitution $t = x^{-2}$ reduces the integral above to $2\int_0^\infty e^{-ax^2}e^{-k/x^2}\mathrm{d}x$, which is found in standard tables such as M. Abramowitz and I. A. Stegun, "Handbook of Mathematical Functions", Dover Publications, New York, N.Y., 1973, p 302, integral 7.4.3. The author is grateful to R. C. Morrison, O. Day, and J. M. Deutch for demonstrating, on separate occasions, the utility of this substitution in connection with integrals containing $t^{-3/2}\mathrm{d}t$.

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Chemistry of the Triplet State of Diazines in Solution Studied by Laser Spectroscopy

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Abstract: Optical excitation at 265 nm of diazines in aqueous and organic solvents was carried out using single pulses of ~15-nsec duration from a frequency quadrupled neodymium glass laser. The technique of kinetic absorption spectrophotometry was used to observe and study the short-lived transient species formed at room temperature. Pyrazine, pyrimidine, pyridazine, quinoxaline, and phthalazine were studied in water, isopropyl alcohol, acetonitrile, and cyclohexane. The transient absorption spectra of these diazines were determined in the wavelength region 230–900 nm. These are assigned, primarily, to triplet states. Their lifetimes in water at 25° are 4.5, 1.4, 29.4, and 21.2 μsec for pyrazine (Pz), pyrimidine (Pm), quinoxaline (Qx), and phthalazine (Pl), respectively. In organic solvents, the triplet lifetimes are generally reduced. The observed triplet states of Pz and Pm are suggested to be (n,π*) in character and are effectively quenched by H atom donors; e.g., $k_q \sim 10^8$ M^{-1} sec^{-1} by isopropyl alcohol. The triplet states of Qx and Pl are predominantly (π,π*) in character and are quenched relatively slowly, $k_q \leq 10^4$ M^{-1} sec^{-1}, by H atom donors. The spectra of the azyl radicals produced from these diazines have been identified. For example, in water the ·PzH and $\cdot PzH_2^+$ radicals are observed. The rate constants for quenching of the triplet states of diazines by O_2, H^+, OH^- ions and by inorganic ions of CTTS character were determined. These and other results are discussed.

It is the "lone-pair" electrons of aromatic nitrogen heterocyclic molecules which usually determine the nature of the radiative and radiationless paths for deactivation of the excited states of these compounds, as well as the photochemical properties of heteromolecules. The electronic absorption spectra and the (n,π*) and (π,π*) nature of the excited singlet and triplet states of diazabenzenes, as well as diazanaphthalenes, have been studied in great detail.[2-11] These molecules exhibit a weak fluorescence but are found to show strong phosphorescence. The diazabenzenes are re-