Diffusion Studies on the Benzyl and Cyclohexyl Radicals in Solution

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Abstract: Diffusion coefficients for the cyclohexyl and benzyl radicals have been measured in cyclohexane at 25° using the photochemical space intermittency method. The average values obtained are $D_{PhCH_2} = 1.1 \times 10^{-5}$ and $D_{C_6H_{11}} = 4.0 \times 10^{-6}$ in units of cm²/sec. Benzyl is the only carbon radical studied which diffuses at a rate equal to that predicted for the parent hydrocarbon. The cyclohexyl radical and all other alkyl radicals studied diffuse much more slowly than expected. The results are interpreted to mean that alkyl radicals interact with solvent much more strongly than does the benzyl radical, even in a relatively inert solvent such as cyclohexane.

Radical combination reactions in solution have been studied by a variety of techniques including flash photolysis,[1] pulsed radiolysis,[2] esr methods,[3] and rotating sector.[4] In the case of hydrocarbon radicals the specific rate constants measured for recombination are usually slightly smaller than would be calculated for a purely diffusion-controlled process using the Smoluchowski equation.[5] A certain element of uncertainty is present in these calculations, however, because they require both a knowledge of the encounter radius for the reaction and the diffusion coefficient of the radicals involved. In the present studies attention is focused upon the problem of obtaining diffusion coefficients for the very reactive free radicals involved in these reactions. It happens that these diffusion coefficients may be determined directly by a special technique known as photochemical space intermittency (PCSI).[6] Thus a primary goal of this research is to obtain diffusion coefficients for highly reactive species which may very well be undergoing recombination at or near the diffusion-controlled rate. These diffusion data may then be used, along with encounter radii deduced from molecular models, to calculate rate constants from the Smoluchowski equation, thus providing a more realistic comparison with experimental rate constants than is now possible.

In the present work the benzyl and cyclohexyl radicals were selected for study on the basis of several considerations. First of all, molecular models of these compounds indicate that, in solution, one may be certain that their shapes are reasonably invariant and roughly that of a disk. In contrast, the *n*-alkyl radicals studied earlier have irregular shapes due to random coiling of the carbon chains and hence the encounter radii assumed are subject to greater uncertainty than for regularly shaped molecules. Of more importance, however, is the fact that, for the benzyl radical, several

independent measurements of the recombination rate constant are available and four independent measurements of the cyclohexyl radical recombination rate constant are known. Also, hydrogen abstraction from the cyclohexane solvent by these radicals is irrelevant in the case of the cyclohexyl radical and negligibly slow in the case of the benzyl.[7] Thus, we can be certain of the identity of the radical whose mobility we are measuring. Finally, it is important that the self-diffusion coefficient of cyclohexane has previously been measured, providing, for the first time, a direct comparison between the diffusion of a free radical and its parent hydrocarbon in the same solvent.

Experimental Section

The subject radicals are produced by the triethyl phosphite–thiol reaction which is a chain process.[8] The reaction is initiated by the photodecomposition of azocyanocyclohexane (AZC) and the rate is measured by the disappearance of thiol. Previous work[8] has shown that if the molar ratio of triethyl phosphite to thiol is sufficiently large, then the rate of thiol disappearance is given by

$$-d[RSH]/dt = k_p[RSH]R_i^{1/2}/k_t^{1/2} \qquad (1)$$

where R_i is the rate of initiation and k_p and k_t are specific rate constants for the reactions

$$R\cdot + RSH \longrightarrow RH + RS\cdot \qquad (2)$$

and

$$2R\cdot \longrightarrow products \qquad (3)$$
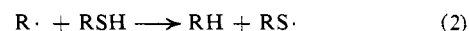
respectively.

In this work the excitation light was introduced to the reaction solution after passing through a space intermittency pattern consisting of opaque regions and translucent spots. The spots are arranged in a hexagonal array each spot having six nearest neighbors and the distance between nearest neighbors being three times the spot diameter.

The theory of this experiment has been discussed in detail elsewhere[6] and the data analysis for this particular system has also been thoroughly described.[9] It is important to recall, however, the contrasting effects of very coarse patterns in which individual spots are much larger than the root mean square (rms) displacement of a radical center during its lifetime and very fine patterns for which individual spots are much smaller than this rms displacement. If, for example, the pattern transmits 10% of the incident light, then,

(1) T. O. Meiggs, L. I. Grossweiner, and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 7986 (1972), and references cited therein.

(2) (a) R. J. Hagemann and H. A. Schwarz, *J. Phys. Chem.*, **71**, 2694 (1967); (b) M. C. Sauer and I. Mani, *ibid.*, **72**, 3856 (1968); (c) M. Ebert, J. P. Keene, E. J. Land, and A. I. Swallow, *Proc. Roy. Soc., Ser. A*, **287**, 1 (1965).

(3) (a) G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 491 (1972); (b) S. A. Weiner and G. S. Hammond, *ibid.*, **91**, 986 (1969).

(4) (a) D. J. Carlson and K. U. Ingold, *ibid.*, **90**, 7047 (1968); (b) R. D. Burkhart, *ibid.*, **90**, 273 (1968).

(5) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, Wiley, New York, N. Y., 1961, p 271.

(6) S. A. Levison and R. M. Noyes, *J. Amer. Chem. Soc.*, **86**, 4525 (1964), and earlier work cited therein.

(7) Methyl radicals abstract H atoms from alkanes (*e.g.*, ethane) with log $A \simeq 8.6$ M^{-1} sec^{-1} and $E_{act} \simeq 10.8$ kcal/mol (see S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 100). Resonance stabilization of the benzyl radical would place $E_{act} \simeq 24$ kcal for H atom abstraction by this radical. Assuming log $A = 8.6$ then at 25° k(abstraction) = 1.3×10^{-9}. To make k as large as 1, E_{act} would have to be 12 kcal, an unreasonably low value.

(8) R. D. Burkhart, *J. Phys. Chem.*, **70**, 605 (1966).

(9) R. D. Burkhart, R. F. Boynton, and J. C. Merrill, *J. Amer. Chem. Soc.*, **93**, 5013 (1971).

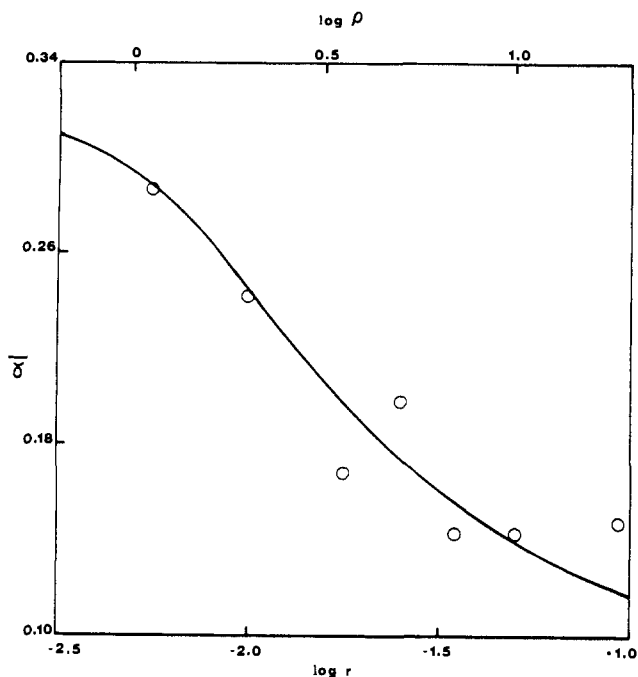Figure 1. PCSI results for the benzyl radical in cyclohexane at 25°. $R_i = 3.5 \times 10^{-11} M \sec^{-1}$.

Figure 2. PCSI results for the cyclohexyl radical in cyclohexane at 25°. $R_i = 5.9 \times 10^{-12} M \sec^{-1}$.

in the coarse pattern limit, the rate when a pattern is in place is only 0.1 of that observed with full light intensity. In the limit of very small spots the effect is the same as decreasing the incident light intensity by a factor of 10 uniformly over the entire solution. Since R_i is directly proportional to the incident light intensity, then, according to eq 1, insertion of a pattern of sufficiently small spots in the incident light beam results in a rate decrease of $10^{-1/2}$.

All of the techniques involved in carrying out these experiments have been described previously including purification of reagents, method of measuring rates, and operation of the optical system.[9] Since $k_p/k_t^{1/2}$ is known for both the triethyl phosphite-α-toluenethiol reaction and the triethyl phosphite-cyclohexanethiol reaction, R_i could be determined directly from rate experiments utilizing full illumination.

Results and Discussion

Figures 1 and 2 summarize the PCSI experiments on the benzyl and cyclohexyl radicals, respectively. Each experimental point represents an average of the runs made with that particular spot pattern and there are a total of 24 rate experiments involved in the cyclohexyl system and 14 for the benzyl system. The solid curve in these graphs represents a theoretically derived relation between $\log \rho$ and $\bar{\gamma}$, where ρ and γ are dimensionless variables. The variable γ is the steady state radical concentration produced when a space intermittency pattern is in place divided by the steady state radical concentration using full illumination. The overhead bar in connection with γ is meant to represent a spatially averaged value.

The dimensionless variable ρ is defined by

$$\rho = (4R_i k_t/D^2)^{1/4} r \tag{4}$$

where D is the diffusion coefficient and r is the distance to any point from the center of a spot.

In Figures 1 and 2 the experimental points were fit to the theoretical curve by a horizontal translation of the entire curve. The shape of the curve is, of course, fixed by theory so it is only the horizontal translation that is involved in curve fitting.
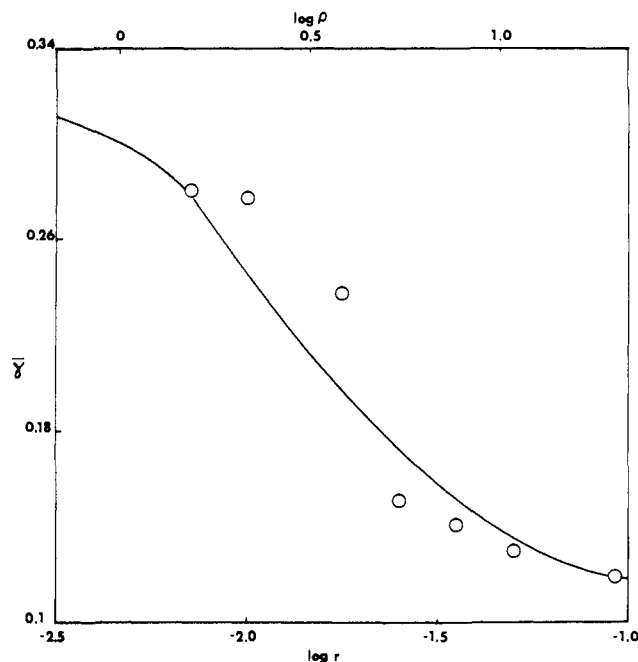
Table I. Summary of PCSI Results for the Benzyl and Cyclohexyl Radicals in Cyclohexane at 25°

Radical	r_1, cm	R_i, $M \sec^{-1}$ $\times 10^{12}$	$D/k_t^{1/2}$, $cm^2 M^{1/2}/\sec^{1/2}$ $\times 10^{10}$
Benzyl	0.0045	35	2.4
Cyclohexyl	0.0047	5.9	1.1

Table I shows the results of this analysis r_1 being the experimentally determined value of r corresponding to $\rho = 1$. The last column of this table gives $D/k_t^{1/2}$ which is the most that PCSI measurements alone can yield. The diffusion coefficient which one quotes is therefore dependent upon a separately determined value for k_t.

Absolute rate constants for radical combination reactions involving carbon radicals have a reputation of poor precision but, as mentioned above, they are necessary for the extraction of diffusion coefficients from the PCSI data. Relative standard deviations in $D/k_t^{1/2}$ values are also fairly large and are calculated to be about 50% for these experiments. In spite of these precison problems, the standard deviations in derived values of the diffusion coefficients are maintained at an acceptably low value primarily for two reasons. First, the reputation of poor precision in k_t values is somewhat undeserved, at least for the cyclohexyl and benzyl radicals. Second, k_t enters the calculation as the square root.

The first point may be demonstrated by the statistical approach of gathering together applicable k_t values for each radical reported in the literature and then calculating a standard deviation. For the cyclohexyl radical k_t values, in units of 10^9 M^{-1} $\sec^{-1}$, are 1.4[4a] and 0.60,[10] by rotating sector experiments using different monitor reactions, and 1.3[2c] and 2.0[2b] by pulse radiolysis studies in different laboratories. The average k_t

(10) R. D. Burkhart, J. Phys. Chem., 73, 2703 (1969).

value is 1.3×10^9 M^{-1} sec^{-1} and the relative standard deviation is 44%. For the benzyl radical in cyclohexane, rotating sector[8] and pulse radiolysis experiments[2a] yield the same k_t value of 2.0×10^9 M^{1-} sec^{-1}. If we include the recent k_t value of 0.68×10^9 M^{-1} sec^{-1} obtained by flash photolysis in methanol,[1] then the average k_t for the benzyl radical is 1.6×10^9 M^{-1} sec^{-1} with a relative standard deviation of 48%.

The second point may be demonstrated by a continuation of this statistical argument. The relative standard deviations in $k_t^{1/2}$ values turn out to be 26 and 28% respectively for the cyclohexyl and benzyl radical. The overall relative standard deviation in the finally calculated diffusion coefficient is the square root of the sum of the squares of the component relative standard deviations. One finds, therefore, that the k_t values contribute 6 and 7% to the relative standard deviations of the derived diffusion coefficients for cyclohexyl and benzyl, respectively. These represent rather minor additions to the estimated standard deviations from the PCSI data. Table II

Table II. Diffusion Coefficients of the Benzyl and Cyclohexyl Radicals in Solution at 25° Assuming Various Values for k_t Measured in Cyclohexane

Radical	k_t, M^{-1} sec^{-1} $\times 10^{-9}$	D,[a] cm^2/sec $\times 10^5$	Ref
Benzyl	2.0	1.1	2a, 10
Cyclohexyl	2.0	0.49	2b
Cyclohexyl	0.60	0.27	10
Cyclohexyl	1.4	0.41	4a
Cyclohexyl	1.3	0.40	2c

[a] The precision estimate for each of these is ±57% of the quoted value.

gives the experimental diffusion coefficients based on these various values of k_t and the data in the last column of Table I. By way of comparison, the Stokes-Einstein diffusion coefficient, eq 5, is calculated to be

$$D = (kT)/(6\pi\eta r) \qquad (5)$$

1.1×10^{-5} cm^2 sec^{-1} for the benzyl radical using 0.0088 P for the viscosity of cyclohexane at 25° and 2.2 Å[4b] for the radius of the benzyl radical. For the cyclohexyl radical a comparison is provided by the self-diffusion coefficient of cyclohexane which is 1.38×10^{-5} cm^2 sec^{-1}.[11]

Using any of the values of k_t for the cyclohexyl radical, the data show that the resulting diffusion coefficient is on the order of one-third to one-fifth of that found experimentally for the cyclohexane molecule. Although this represents a rather marked difference, it should be pointed out that all of the measured diffusion coefficients for the linear alkyl radicals in cyclohexane[9] are significantly smaller than would be expected for the corresponding parent alkane (see Table III). It might be suspected that, through some experimental artifact, the methods used here always yield lower than expected diffusion coefficients; however, the results obtained for the benzyl radical (*vide infra*) make such a suspicion untenable. In view of the relative errors associated with the diffusion measurements and with the inde-

(11) D. W. McCall, D. C. Douglass, and E. W. Anderson, *J. Chem. Phys.*, **31**, 1555 (1969).

Table III. Experimentally Determined Diffusion Coefficients for Various Carbon Radicals, D_e, Compared with Those Expected for the Parent Hydrocarbon, D_p[a]

Radical	D_e	D_p	$R = D_p/D_e$
Benzyl	11	11	1.0
Cyclohexyl	4.0	14	3.5
1-Propyl	8.0	25	3.1
1-Pentyl	0.8	22	28
1-Dodecyl	1.6	11	6.9
1-Octadecyl	2.7	7.8	2.9

[a] Diffusion coefficients in units of 10^{-6} cm^2 sec^{-1}.

pendently measured value of k_t, an average value of D for the cyclohexyl radical of 0.4×10^{-5} cm^2 sec^{-1} will be assumed for purposes of discussion.

In spite of the assumption made in calculations of diffusion-controlled rate constants by the Smoluchowski equation as discussed by Noyes,[12] it is of interest to utilize the experimentally obtained diffusion coefficients in such a calculation to see how well this theoretical relation reproduces k_t values found by the various techniques discussed above. For the cyclohexyl radical, molecular models suggest that an encounter radius of 3 Å is a reasonable value and this leads to a calculated rate constant of 9×10^8 M^{-1} sec^{-1}. This is well within the estimated standard deviation of the average k_t of 1.3×10^9 M^{-1} sec^{-1} calculated for this radical from earlier work as discussed above.

The diffusive behavior of the benzyl radical is quite unlike that found for any of the alkyl radicals studied to date. The diffusion value quoted in Table II is larger than is found for any alkyl radical. Furthermore, there is the remarkable fact that the Stokes-Einstein diffusion coefficient for the benzyl radical agrees exactly with the experimentally obtained value assuming $k_t = 2.0 \times 10^9$ M^{-1} sec^{-1}. Another manifestation of the singular nature of this radical concerns the D_p/D_e ratio (Table III) which, within experimental error, is equal to 1 only for the benzyl radical.

Again it is of interest to test the predictions of the Smoluchowski equation utilizing the experimental diffusion coefficient of 1.1×10^{-5} cm^2 sec^{-1} and 4.4 Å as the encounter radius. In this case the diffusion-controlled rate constant is calculated to be 3.7×10^9 M^{-1} sec^{-1}, which is somewhat larger than the experimental values but indicates that benzyl radical recombination occurs at nearly every encounter. This conclusion is in contrast to that reached directly on the basis of k_t values obtained by flash photolysis.[1]

For purposes of comparison, each radical species for which the diffusion coefficient has been measured, both in the present work and in previous studies,[9] has been assigned either a calculated diffusion coefficient based on Stokes law or, as in the case of cyclohexane, has a known diffusion coefficient for the parent hydrocarbon. Diffusion coefficients of this type are what one would expect for the relatively unreactive parent hydrocarbon and, for the remainder of this discussion, we symbolize them by D_p. Using D_e to symbolize experimentally determined diffusion coefficients for the various free radicals, it is useful to consider the ratios $R = D_p/D_e$ for each radical. These are summarized in Table III.

The ratio obtained for the 1-pentyl radical seems to be far out of line compared with the remaining results

(12) R. M. Noyes, *Progr. React. Kinet.*, **1**, 130 (1961).

and indicates that a major unresolved problem exists in the measurements made on this species. Perhaps the most striking feature of the data of Table III is the fact that R is significantly greater than 1 for all of the alkyl radicals but, within experimental error $D_p = D_e$ for benzyl.

The PCSI method for obtaining diffusion coefficients is relatively new and untried. The contribution to the uncertainties in final values due to precision difficulties in the PCSI experiments and arising from uncertainties in the k_t values used has been discussed above. In spite of these associated uncertainties, the observed ratios, R, for alkyl radicals are too large to dismiss as due to experimental error.

In addition, a demarcation in R values is exhibited which corresponds with a demarcation in the chemical nature of the radicals involved. That is, those species for which the unpaired electron is localized at a particular carbon atom have $R > 1$, whereas in the benzyl radical for which the unpaired electron is delocalized $R = 1$ within experimental error.

A process which can account for these observations is immediately suggested when one considers the relatively large potential for reactivity inherent in those species containing a localized unpaired electron. Although hydrogen abstraction from solvent molecules by radicals does not compete significantly with that represented by eq 2, it may be expected that many collisions will involve at least incipient formation of a C–H–C three electron three center system. In the liquid phase, molecules are thought to be in a nearly continuous state of collision but, in the case of alkyl radicals, the collisions would likely be quite inelastic if such a radical–solvent interaction were operative. A high collision frequency coupled with this proposed radical–solvent interaction leads to the notion that a large fraction of the radicals in solution at any time would not exist as independent species. Using this idea, it is clear that cyclohexane cannot be thought of as an inert solvent and that one cannot really conceive of alkyl radical diffusion in cyclohexane in the same way that one pictures the diffusion of a stable molecule.

A logical extension of this argument would indicate that for a radical in which the unpaired electron is extensively delocalized then radical–solvent interactions would be considerably less energetic and interference to normal Brownian motion from this source would be proportionately reduced. Thus, the experimental diffusion coefficient for the benzyl radical is very near the "normal" value expected for the nonreactive parent molecule. In essence then, it is being suggested here that the alkyl radicals in solution are not really free radicals in the sense of translational freedom. They are instead associated with solvent molecules to a large

extent so that Stokes–Einstein calculations which utilize the radius of a single radical will always overestimate mobility because the effective migrating unit is a larger radical–solvent aggregate.

Earlier work on the solvent effects associated with reactions 2 and 3 indicated that alkyl radicals interact more strongly with benzene than with cyclohexane.[10] In their study of the effect of solvents on radical combination reactions, Hammond and Weiner[3b] came to the same conclusion and more recent thermodynamic studies by Bentrude and MacKnight[13] reinforce this view. Another example of strong interactions between benzene and odd-electron species involves chlorine atoms.[14–17] Judging from these chemical observations it seems apparent that the energies associated with at least some radical–benzene interactions are comparable with the activation energies of the comparison chemical processes, probably a few kilocalories in most cases. Since translational energies are relatively much lower on the energy scale (i.e., on the order of RT), diffusion coefficients are likely to be more sensitive to weak radical–solvent interactions than most chemical processes would be (except perhaps radical combination reactions) and, therefore, in the present study it is suggested that even the radical–cyclohexane interaction is energetic enough to influence radical mobility.

Not all of the observations associated with values of D_p/D_e may be accounted for by the mechanism proposed above. For example, this ratio is 3–6 for most of the alkyl radicals studied but is 28 for the pentyl radical. A satisfactory explanation for this latter result is still to be found. Nevertheless, the main features of the diffusion data gathered to date fit into the mechanistic framework outlined here. Furthermore, the chemical processes proposed to account for radical solvent interactions are not at all new but instead make use of the well-known model of a potentially reactive encounter in which the reactive partners generally have insufficient energy to form products moving only a short distance along the reaction coordinate before returning to the original reactants. For such a process to influence radical mobility it is only necessary that collisions be sufficiently frequent and encounters be sufficiently long lived so that a relatively large fraction of radicals present at any time are associated with the solvent.

(13) W. G. Bentrude and A. K. MacKnight, *J. Amer. Chem. Soc.*, **92**, 4357 (1970).
(14) M. L. Poutsma, *ibid.*, **87**, 2161 (1965).
(15) M. L. Poutsma and R. L. Hinman, *ibid.*, **86**, 3807 (1964).
(16) C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959).
(17) G. A. Russell, *ibid.*, **80**, 4987 (1958).