An interesting conclusion concerning the kinetic reasons for the observed predominance of reaction 10 over 9 can be formulated from the present data for reaction 5 and the analogous published data for reaction 11. Since the pairs of forward and reverse re-

$$CH_3 + C_3H_6 \longrightarrow sec\text{-}C_4H_9 \qquad (10)$$

$$sec\text{-}C_4H_9 \longrightarrow CH_3 + C_3H_6 \qquad (11)$$

actions 10 and 11 and 5 and 9 should have the same transition states, then we would expect relation 12 to hold. Taking A_5 from the present data, A_{11} from an

$$\Delta S_5° - \Delta S_{11}° = R \ln (A_5A_{10}/A_9A_{11}) \qquad (12)$$

average of the two published estimates of this quantity (2.1×10^{15} from Calvert and Gruver[17] and 0.62×10^{15} sec^{-1} from Lin and Laidler[18]), and reasonable entropy data for the isobutyl and *sec*-butyl free radicals,[19] then from relation 12 the ratio of A_9 to A_{10} can be estimated.

$$A_9/A_{10} \cong 4.0 \times 10^{-4}$$

These results suggest that the large preference shown for the *sec*-butyl over isobutyl radical formation as methyl adds to propylene in reactions 10 and 9, respectively, is largely a consequence of the larger preexponential factor for reaction 10. The activation energy difference, $E_9 - E_{10}$, is probably small since the assumption of $E_9 \cong 8$ kcal/mole, a value near equal to that found for E_{10} by Miyoshi and Brinton (8.8 kcal/mole),[20] has been shown earlier to provide a consistency between the present kinetic data and reasonable thermal data. We are currently attempting to measure the ratio k_9/k_{10} directly to test these conclusions.

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[17] (a) J. G. Calvert, *Chem. Rev.*, **59**, 569 (1959); (b) J. T. Gruver and J. G. Calvert, *J. Am. Chem. Soc.*, **78**, 5208 (1956); **80**, 3524 (1958).

[18] M. C. Lin and K. J. Laidler, *Can. J. Chem.*, **45**, 1315 (1967).

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Absolute Rate Constants for the Bimolecular Reaction of Radical Pairs in Solution. Benzyl and Pentyl Radicals

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Abstract: Absolute rate constants for the combination–disproportionation of pentyl radicals and for the combination of benzyl radicals have been measured in benzene at 25° in order to test the utility of the free-radical reaction between triethyl phosphite and mercaptans as a monitor for steady-state alkyl radical concentrations and to provide preliminary data with which theories of diffusion-controlled reactions might be tested for chain-like radicals in solution. The rotating sector method has been used yielding $k_{2C_5H_{11}} = 1.0 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ and $k_{2C_6H_5CH_2} = 4.1 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. Both experimental values are smaller than those calculated using the assumption that there is negligible difference between diffusion coefficients of the radicals and the parent hydrocarbons.

Although a number of studies have been carried out to measure absolute combination (and disproportionation) rate constants of polymeric radicals in solution, very little has been done to evaluate such rate constants for small hydrocarbon radicals; in fact, the benzyl radical, studied in relatively viscous solvents by pulsed radiolysis[1] and flash photolysis,[2] and the ethyl radical, studied by intermittent electron irradiation[3] at −177 to −140°, appear to be the only previous examples. The motivation for undertaking the present work derives from questions concerning the applicability of the theory of diffusion-controlled reactions to recombination[4] processes involving pairs of chain-like radicals in solution such as linear alkyl radicals. While it is well known that polymeric radicals recombine at smaller rates than their lower molecular weight homologs, the details of the recombination process are not well understood in spite of several theoretical and experimental investigations.[5] Data on recombination rate constants of linear alkyl radicals which are monodisperse in terms of molecular weight would be useful at least to the extent that effects of radical size could be evaluated. Indeed, the effects of most controllable factors on these reactions are virtually unexplored.

Although the studies of hydrocarbon radicals mentioned above have yielded useful information, the techniques used there are not well suited to the sort of investigation proposed here. On the one hand, high-energy electron irradiation lacks selectivity and, on the other, the spectrophotometric monitoring of alkyl radical concentrations is not feasible because of interfering absorption by most solvents. The object of

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[1] R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, **56**, 1187 (1960).

[2] G. Porter and M. W. Windsor, *Nature*, **180**, 187 (1957).

[3] R. E. Fessenden, *J. Phys. Chem.*, **68**, 1508 (1964).

[4] Although the bimolecular reaction of two pentyl radicals undoubtedly yields disproportionation as well as combination products, the term recombination will be used here to describe the radical–radical reaction irrespective of products formed.

[5] For a recent review, see A. M. North, *Quart. Rev.* (London), **20**, 421 (1966).

the present work, therefore, has been to find and develop a method which is as generally applicable as possible for the study of radical recombination reactions in solution, particularly those processes involving alkyl radicals.

It was initially thought that the rotating sector method could be applied in this investigation. To do so, however, it is necessary that a photochemically initiated free-radical chain reaction be found for which the major chain-carrying species is the hydrocarbon radical of interest and for which the termination process is second order with respect to this radical. Recent experiments[6] have shown that these general conditions prevail for the photochemically initiated reaction between 1-pentanethiol and triethyl phosphite and, as will be seen presently, for a similar reaction in which α-toluenethiol is substituted for 1-pentanethiol. This reaction, discovered by Hoffman and coworkers,[7] was later characterized as a radical chain reaction by Walling and Rabinowitz.[8] When the molar ratio of triethyl phosphite to thiol is sufficiently large, the rate of thiol disappearance has the form

$$\frac{-\mathrm{d[RSH]}}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{RSH}](R_\mathrm{i}/k_\mathrm{t})^{1/2} \qquad (1)$$

where k_p and k_t are specific rate constants for the reactions

$$\mathrm{R} + \mathrm{RSH} \xrightarrow{k_\mathrm{p}} \mathrm{RH} + \mathrm{RS} \qquad (2)$$

$$2\mathrm{R} \xrightarrow{k_\mathrm{t}} \text{products} \qquad (3)$$

At the small concentrations of 2,2′-azobisisobutyronitrile (ABN) used in this work as initiator, the rate of initiation, R_i, is given by the equation

$$R_\mathrm{i} = 2.303E\phi I_0[\mathrm{ABN}]l \qquad (4)$$

where $E = 9.70$ is the decadic extinction coefficient of ABN,[9] I_0 is the incident light intensity, ϕ is the fraction of radicals which escape the solvent cage per quantum of light absorbed, found previously[6] to be 0.158, and l is the optical path length of the reaction cell. A stationary-state treatment of the reaction scheme

$$\mathrm{ABN} \longrightarrow 2\mathrm{A} + \mathrm{N_2} \qquad (5)$$

$$\mathrm{A} + \mathrm{RSH} \longrightarrow \mathrm{RS} + \mathrm{AH} \qquad (6)$$

$$\mathrm{RS} + \mathrm{P(OEt)_3} \longrightarrow \mathrm{R} + \mathrm{SP(OEt)_3} \qquad (7)$$

followed by propagation and termination as in eq 2 and 3 yields a rate expression identical with that found experimentally.

Thus, it appears that this reaction meets the requirements for use of the time-intermittent illumination technique, and the present work is intended not only to demonstrate the utility of this system for the study of two particular hydrocarbon free radicals, differing markedly in skeletal structure and chemical reactivity, but also to obtain data with which the theory of diffusion-controlled reactions might be further tested. The choice of 1-pentanethiol was made since earlier work on the kinetics of the monitoring reaction used this mercaptan. Because of the availability of information from earlier studies on the benzyl radical, it was also decided that α-toluenethiol should be included in this initial study for comparative purposes. Work on combination–disproportionation rate constants of several other linear alkyl radicals is currently in progress and will be reported in due course.

Experimental Section

Triethyl phosphite, 1-pentanethiol, ABN, and solvent benzene were purified as previously described.[6] A 20-cm Vigreux column was used to vacuum distil α-toluenethiol (Eastman) using a nitrogen purge. A center cut boiling at 98.5° (40 mm) was retained, $n^{25}\mathrm{D}$ 1.5738.

Reactions were carried out in a Pyrex cylindrical absorption cell (American Instrument Co.) having optically plane windows and an optical path length of 50 mm. The cell had two parallel radial outlets on the same side of the cylinder. One of these was sealed to the side of a Pyrex test tube, the top of which had been sealed to a ground-glass joint. The other opening was sealed to a socket joint.

In preparing for a run, the reactants were weighed into a 25-ml volumetric flask with final dilution to the mark with solvent. Slightly less than 15 ml of this solution was then introduced into the test tube. An adapter and stopcock were attached to the ground-glass joint at the top of the test tube so that the apparatus could be attached to a vacuum line. A ball joint with a sealed end was connected to the socket arm of the reaction cell. The solution was then out-gassed using at least three freeze–thaw cycles, and after warming to room temperature the apparatus was removed from the vacuum system and tilted, allowing the solution to run into the cell. The apparatus was then placed in a thermostated box constructed so that reproducible placement of the cell in the light beam could be achieved. The reaction was then run for the desired length of time at 25 ± 0.5° using either steady or time-intermittent light. A similar procedure, except for degassing, was used in the actinometry experiments.[10]

A Hanovia mercury arc lamp (Model No. 30620) was used as the light source. The light beam was passed through a glass optical collimating system, a Corning No. 5840 filter, and the front window of the Pyrex reaction vessel before traversing the reaction solution. Thus, the major component of the transmitted beam was due to the mercury 366-mμ emission. The only component of the reaction solution which absorbs in this wavelength range is ABN.

When the light source was brought to a focus on the rotating sector, the image produced was sufficiently broad that a considerable transition time was found during beam cutoff. This, of course, is undesirable since rectangular light pulses are required. A slit was therefore inserted on the lamp side of the sector which passed a beam of light 1.5 mm in width, and the sector was set to rotate in a plane about 2 mm away from the plane of the slit. To check the rectangularity of the resulting light pulses, a cadmium sulfide photoconductive cell was mounted in a position which would normally be occupied by the rear of the reaction cell. The decay of a 60-Hz signal across this cell during the transition from light off to light on was then measured using an oscilloscope. A transition time of about 20 msec was found when the sectored disk was rotating at 5 rpm. Transition times for other sector speeds were readily calculated from this result and, using an analysis worked out by Burns and Dainton,[11] it was estimated that the actual integrated radical concentration over a light plus dark cycle deviated from the ideal case by no more than 0.2% for any of the sector speeds used. It was assumed that this represented sufficiently rectangular pulsing.

Two different sectored disks were used in these experiments. One disk had a single 90° sector cut out, and the other had opposing 45° sectors removed. Thus, the ratio of dark to light periods was always 3:1. Synchronous motors (Hurst Mfg. Co.) were used to drive these disks. All of the motors used (varying in speed from $^1/_3$ to 120 rpm) had exactly the same type of mounting frame; therefore, a single motor mount attached to the optical bench was sufficient to allow free interchange of motors without disturbing the rest of the optical system.

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[7] F. W. Hoffman, R. J. Ess, T. C. Simons, and R. S. Hanzel, *J. Am. Chem. Soc.*, **78**, 6414 (1956).

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[11] W. G. Burns and F. S. Dainton, *Trans. Faraday Soc.*, **46**, 411 (1950).

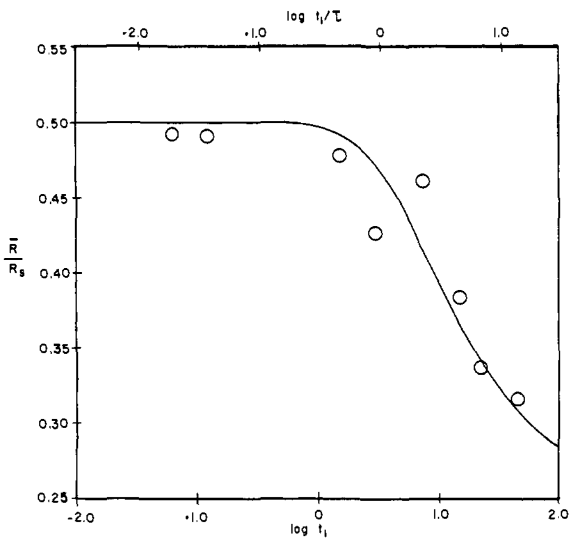

Figure 1. Graph of the ratio of average pentyl radical concentrations during intermittent ($\bar{R}$) and steady (R_S) illumination *vs.* log t_l/τ (upper scale) and log t_l (lower scale).

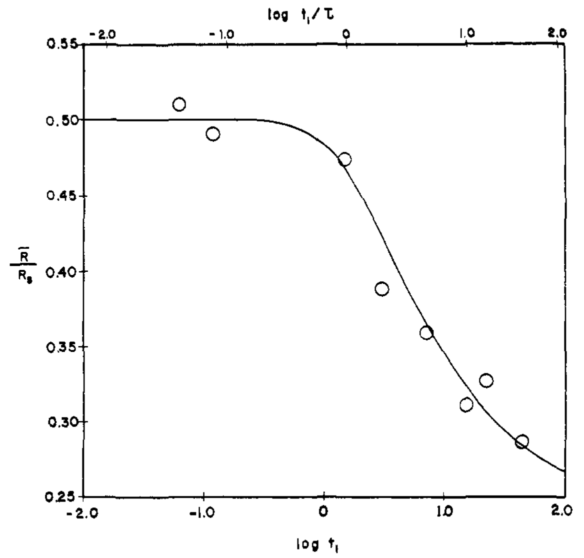

Figure 2. Graph of the ratio of average benzyl radical concentrations during intermittent ($\bar{R}$) and steady (R_S) illumination *vs.* log t_l/τ (upper scale) and log t_l (lower scale).

Unappreciated in the early stages of this work was the need, not only for good collimation of the light beam, but also for avoiding inhomogeneity over the cross section of the beam. It was also found that the 90° sectored disk did not rotate at a uniform speed until it was weighted along the edge of the sector cut-out with solder. Both of these problems gave rise to some misleading early results.

It was found necessary to use the maximum light intensity available from the lamp and ABN concentrations of about 2.5×10^{-5} *M* in order to reduce the rate of thermal initiation to less than 1% of the photoinitiated rate. The residual dark reaction was considered negligible and no correction for it was attempted.

Reaction rates were determined by the analysis of mercaptan present before and after a run. Potentiometric titration of the mercaptan with mercuric nitrate according to the method of Fritz and Palmer was used.[12]

Results and Discussion

Before attempting to measure the recombination rate constant for benzyl radicals in solution, it was necessary to conduct rate experiments using light of constant intensity in order to see whether eq 2–7 were valid for the reaction of α-toluenethiol with triethyl phosphite. Initially an experiment was carried out to confirm the over-all course of the reaction as reported by Hoffman and coworkers.[7] A mixture consisting of 0.012 mole each of triethyl phosphite and α-toluenethiol together with 5×10^{-4} mole of ABN was degassed and then heated *in vacuo* for 2 hr at 75°. Analysis of the reaction mixture on the gas–liquid partition chromatograph showed two major elution peaks plus two others which were just detectable. The two major components were separated by distillation and, in agreement with earlier work, were found to be toluene and triethyl phosphorothioate by infrared analysis. The glpc retention times of the minor components corresponded to neither the mercaptan nor the phosphite. They are perhaps products of radical combination reactions, but no attempt at their further identification was made.

Rate constants calculated using the integrated form of eq 1 for the photoinitiated reaction between α-toluenethiol and triethyl phosphite are presented in Table I along with a summary of experimental conditions. In these experiments the mercaptan and triethyl phosphite concentrations as well as the intensity of absorbed light are all varied in excess of a factor of 7. Reasonably constant values of $k_p/k_t^{1/2}$ are obtained over this range of concentrations, the average deviation from the mean being about 3.2%. This is taken to be good evidence that 1-pentanethiol and α-toluenethiol behave similarly in this reaction so that the mechanism discussed above appears, therefore, to be equally valid for both mercaptans. An interesting difference in the kinetics of these two reactions was noted, however. Previous work showed that initial concentration ratios of triethyl phosphite to 1-pentanethiol of at least 10:1 were required in order to be certain that the major chain-carrying species was the pentyl radical. For the case of α-toluenethiol this ratio can be lowered to about 2:1 with no change in the observed rate constant outside of experimental error. This would indicate that the ratio of rate constants for step 7 to step 2 is greater in the case of α-toluenethiol. This is the result which would probably be predicted in view of the relative stability of the benzyl *vs.* the pentyl radical.

Table I. Rate Constants Calculated from the Integrated Form of Eq 1 for the Photoinitiated Reaction between α-Toluenethiol and Triethyl Phosphite at 25° and Varying Reactant Concentrations

$(ATT)_0$,[a] $M \times 10^3$	$(TEP)_0$,[b] $M \times 10^2$	I_a, einsteins/l. sec $\times 10^{11}$	$k_p/k_t^{1/2}$, $(M^{-1}\,sec^{-1})^{1/2}$
5.8	5.06	5.91	0.844
27.2	37.3	11.9	0.842
15.9	10.1	15.1	0.807
20.0	37.5	59.1	0.815
25.2	38.8	59.1	0.810
28.4	6.11	59.6	0.801
53.4	13.5	61.6	0.720
		Av	0.806
		Av dev	0.026

[a] α-Toluenethiol at zero time. [b] Triethyl phosphite at zero time.

The results of rotating-sector experiments for the 1-pentanethiol and α-toluenethiol reactions are shown in Figures 1 and 2, respectively. The quantities $\bar{R}$ and

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(12) J. S. Fritz and T. A. Palmer, *Anal. Chem.*, 33, 98 (1961).

R_s represent average radical concentrations under conditions of intermittent and steady illumination. For an experiment lasting t_e seconds

$$\bar{R} = \frac{1}{t_e}\int_0^{t_e}[\mathrm{R}]\mathrm{d}t \tag{8}$$

where [R] is the instantaneous radical concentration. Also, R_s is essentially independent of time in view of the time scale considered here and the small fraction of initiator decomposed in a given experiment. From the integrated expression for the rate of step 2, one finds

$$\frac{\bar{R}}{R_s} = \frac{t_e \ln [\mathrm{RSH}]_0'/[\mathrm{RSH}]'}{t_e' \ln [\mathrm{RSH}]_0/[\mathrm{RSH}]} \tag{9}$$

where subscript zero denotes initial mercaptan concentrations, and primes indicate values for intermittent light experiments carried out at the same rate of initiation as the steady-light experiments. Most of the experimental points shown in Figures 1 and 2 were obtained at a constant value of absorbed light intensity. Small deviations occurred because of differences in the weight of initiator used from run to run. In these cases a horizontal correction was applied shifting the point right or left according to whether $\log (I_{ar}/I_a)^{1/2}$ is positive or negative, thus normalizing the data to a reference intensity I_{ar}. For 1-pentanethiol, $I_{ar} = 1.36 \times 10^{-10}$ einstein/l. sec and for α-toluenethiol $I_{ar} = 1.70 \times 10^{-10}$ einstein/l. sec.

The solid curve in Figures 1 and 2 is a graph of $\bar{R}/R_s$ *vs.* $\log t_l/\tau$, where t_l is the duration of a light flash in seconds and τ is the average lifetime of radical centers. This is the curve obtained from the theoretical treatment of the rotating sector experiment and was constructed from the tabulation presented in the review article of Burnett and Melville.[13] In both figures the theoretical curve has been horizontally shifted to give the best fit to the experimental data so that a value of $\log t_l/\tau$ can be found for any value of $\log t_l$ (given on the lower scale in these graphs). This procedure establishes the value of τ at the given rate of initiation. From the well-known relation

$$\tau = \frac{1}{2(k_t\phi I_a)^{1/2}} \tag{10}$$

the absolute rate constant for radical combination is found. The results are summarized in Table II. The k_t values reported here are defined by the equation

$$\frac{-\mathrm{d}[\mathrm{R}]}{\mathrm{d}t} = 2k_t[\mathrm{R}]^2 \tag{11}$$

Table II. Average Radical Lifetimes and Recombination Rate Constants for Pentyl and Benzyl Radicals at 25° in Benzene

Radical	ϕI_a, M sec^{-1}	k_t, M^{-1} sec^{-1}	τ, sec
Pentyl	2.15×10^{-11}	$1.0 \pm 0.3 \times 10^9$	3.4
Benzyl	2.69×10^{-11}	$4.1 \pm 1.2 \times 10^9$	1.5

As expected, both of the experimental rate constants are quite large and of the order of magnitude usually found for diffusion-controlled reactions. It is, therefore, interesting to compare these rate constants with those which would be predicted from the theory of diffusion-controlled reactions.[14] Calculated rate constants are obtained from the equation

$$k_{\text{calcd}} = \frac{4\pi r D_{\text{rel}}(N/1000)}{1 + 4\pi r D_{\text{rel}}(N/1000k_c)} \tag{12}$$

where, for reactions of like radicals, D_{rel} is the diffusion coefficient of the radical of interest in the appropriate solvent and r is the collision diameter for the reacting pair. The factor $N/1000$ converts the rate constant to units of M^{-1} sec^{-1}, and k_c is the rate constant which would be calculated if there were an equilibrium distribution of potential reactants and is calculated from the kinetic theory of gases. The diffusion coefficients of reactant radicals are approximated here by diffusion coefficients of the parent hydrocarbons. Recent calculations[15] have shown that the Kirkwood equation[16] for obtaining frictional forces of chain-like molecules in solution predicts diffusion coefficients in benzene which differ from experimental values by about 10% for *n*-pentane through *n*-dotriacontane. It is noteworthy that the calculation assumes the same segmental frictional force for end methyl groups and internal methylene groups. Therefore, unless there is a large difference in potential energy of interaction for hydrocarbon–solvent *vs.* radical–solvent, the assumed radical diffusion coefficients should be sufficiently accurate for present purposes. Unfortunately, there appear to be no measurements of the diffusion coefficient of toluene in benzene, and so a value was interpolated graphically from a plot of the diffusion coefficient *vs.* the reciprocal of the solvent viscosity for a series of diffusion measurements carried out in *n*-alkanes.[17] The encounter diameter for pentyl radicals was set equal to the root-mean-square end-to-end distance of pentane calculated by methods described by Flory[18] and using parameters summarized in previous work.[15] The encounter diameter of benzyl radicals was estimated from bond distances and angles. It turns out that the estimated encounter diameters are precisely the same for these two radicals at 4.4 Å. Also, the estimated diffusion coefficients differ by only 0.1×10^{-5} cm^2/sec for these two species. Since one could not hope to discern the effect of such a small difference at the present time, the same value of 2.4×10^{-5} cm^2/sec has been taken as the estimated diffusion coefficient for both radicals. Therefore, the calculated value of k_c is 7.7×10^{10} M^{-1} sec^{-1}, and the calculated diffusion-controlled rate constant is 7.2×10^9 M^{-1} sec^{-1}. Thus, benzyl radicals recombine with a specific rate of slightly greater than half of the calculated value, while a discrepancy by a factor of 7 is observed for the recombination of pentyl radicals.

Even though benzyl radicals recombine at a rate of less than the theoretical value, it appears that the process is nevertheless diffusion controlled judging from its viscosity dependence. Thus, Porter and Windsor[2] report that although they could measure the decay of benzyl radicals in viscous solvents such as paraffin oils,

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the reaction was too fast to measure in hexane. Also, in a mixed solvent system with a viscosity of 55 cP, the data of McCarthy and MacLachlan[1] yield a rate constant of 3.3×10^8 M^{-1} sec^{-1} when the extinction coefficient of benzyl radicals[19,20] is set equal to 18,000 M^{-1} cm^{-1} and the rate constant is defined as in eq 11. In the much more fluid solvent used here, the rate constant is over an order of magnitude larger. It is interesting to note that the recombination rate constant for iodine atoms in CCl_4 has also been found to be about one-half as large as the theoretical value.[21]

The failure of the theory to accurately predict the recombination rate constant for pentyl radicals was certainly unexpected, particularly with respect to the magnitude of the discrepancy. For the reactive site of the pentyl radical to be sterically hindered would require successive *gauche* rotations of adjacent carbon–carbon bonds for which the rotations are opposite in sign. The energy of such a rotational state is about 2600 cal greater than that of the *trans–trans* configuration[22] and therefore has a very low probability of occurrence. Thus, steric effects resulting from intramolecular shielding of the reaction site are probably not too important here. It is possible that the potential energy of interaction between pentyl radicals and benzene is much greater than between pentane and benzene. As was mentioned above, this could seriously affect the assumptions made in estimating radical diffusion coefficients. It should also be noted that application of a spin correction term of a factor of 4 would decrease the calculated rate constant to 1.8×10^9 M^{-1} sec^{-1}, giving much better agreement of the results for pentyl radicals with the calculated rate constant. Although it is true that three collisions out of four will lead to a triplet state and hence to no bond formation for the case of small alkyl radicals,[23] it is also evident that the solvent cage model for solution reactions implies that once two radicals have become nearest neighbors they will undergo several collisions before diffusing apart. Thus, spin correction may be required here but it is by no means certain that the correction term is as large as 4. It appears, therefore, that the recombination of alkyl radicals in solution is not a simple process and that, in addition to the effects of molecular size, measurements of radical diffusion coefficients and the evaluation of solvent effects are necessary in order to provide a clearer picture of the reaction mechanism.

Additional information obtainable from these results are values of the rate constant k_p of eq 2. The average value of $k_p/k_t^{1/2}$ for the pentyl radical system found in this work is 2.24 so that k_p is 7.1×10^4 M^{-1} sec^{-1} for the abstraction of the thiol proton by a pentyl radical. The analogous rate constant for the benzyl radical system is obtained from the data of Table I and the rate constant for benzyl radical recombination. As would be expected, a smaller value of 5.1×10^4 M^{-1} sec^{-1} is found for thiol hydrogen abstraction by a benzyl radical.

It is noteworthy that no basic difficulties with the monitoring reaction have been found at this point. Better precision in rate measurements could be obtained if the reaction were followed continuously, but no suitable analytical procedure has been uncovered which would make this possible; however, spectrophotometric analyses may prove feasible in solvents other than benzene. Therefore, the additional experimentation which will be required in order to gain a better understanding of alkyl radical recombination reactions can probably be most simply accomplished by use of the mercaptan–triethyl phosphite monitoring reaction.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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