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Disproportionation–Combination Reactions of Caged Geminate Radical Pairs Formed from the Photodecomposition of 2,2′-Azoisobutane. Anisotropic Reorientation of *tert*-Butyl Radicals in Viscous Media and Birth Effects in Very Viscous Media

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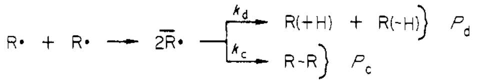
Abstract: The solvent viscosity dependence of the self-termination reactions of *tert*-butyl radical pairs generated from the photolysis of 2,2′-azoisobutane, in a number of inert solvents admixed with thiophenol, shows a linear relationship between the cage efficiency, 1/cage yield, and fluidity, $1/\eta$, of the solvent. The viscosity dependence of the ratio of disproportionation/combination rate constants, k_d/k_c, for these cage reactions was compared to the values observed for the reactions of encounter pairs generated by the photolysis of di-*tert*-butyl ketone. At viscosities between 0.5 and 2.7 cP the k_d/k_c ratios obtained for geminate radical pairs were the same as those obtained from the reaction of the encounter pairs, while at higher viscosities of 12–808 cP the orientation of the geminately formed radicals at birth appeared to bias the radicals to undergo a higher proportion of combination.

In a recent study of the photodecomposition of 2,2′-azoisobutane (AIB) in mixtures of the solvent toluene or a variety of substituted toluenes with thiophenol-*d* added, as an effective scavenger for "escaped" radicals, the *tert*-butyl radicals produced were found to undergo extensive combination and disproportionation reactions within the solvent cage.[1] The cage efficiency (1/cage yield) of the combination–disproportionation reactions was found to be a linear function of the fluidity ($1/\eta$) of the media over a range of solvent viscosities,[2] η, from 0.5 to 3.5 cP. It was noted that the disproportionation to combination ratio, k_d/k_c, did not appear to be constant from solvent system to solvent system and the variation (k_d/k_c = 4.6–9.2) was attributed to the experimental difficulty encountered in the analysis of the small amounts of combination product, 2,2,3,3-tetramethylbutane, produced. However, at about the same time Fischer showed, in a study of the photolysis of di-*tert*-butyl ketone, that k_d/k_c is strongly dependent on solvent viscosity.[4] In a previous paper[5] Fischer had shown, also from the study of the photolysis of di-*tert*-butyl ketone, that the self-termination rate constant k_1, ($k_c + k_d$), of *tert*-butyl radicals, R·, in solution is governed by translational diffusion, i.e., every encounter of two "free" radicals, that forms a caged pair which has the proper spin orientation results in the formation of products; isobutane, R(+H); isobutylene, R(−H); and 2,2,3,3-tetramethylbutane, R–R. The product ratios, P_d/P_c, produced from the reactions were found to be strongly coupled to the viscosity of the media.[4] An elegant collision model was developed which accounts for the viscosity dependence of the P_d/P_c ratios by assuming that while a great majority of the collisions occurring within encounter pairs are unproductive the distribution of the successful (i.e., product forming) reactions is controlled by the anisotropic reorientation of the radicals in a solvent cage formed after encounter. The model for the reaction of two *tert*-butyl radicals depends on partitioning the surface of a planar (or rapidly inverting pyramidal) radical. The surface, depicted as an oblate ellipsoid (see Figure 1), can be pictured as having nonreactive N zones (~90%), reactive C zones leading to combination (~5%), and reactive H zones leading to disproportionation (~5%). Reorientation of one of the collision partners, relative to the C zone of its reaction partner, leads to either combination (**CC** configuration) or disproportionation (**CH** configuration) products whereas the **CN** configuration does not lead to products (see Figure 1). Reorientation about the axis parallel to the p orbital affects only **CH** or **CN** configurations and can only lead to disproportionation products via **CH** interaction. This reorientation process is not greatly affected by the solvent viscosity since only a minimal amount of solvent is displaced by this motion. Reorientation about the axis perpendicular to the p orbital, which leads to combination product, is strongly coupled to the viscosity of the media, since because of the proposed shape of the radical this motion displaces a maximum amount of solvent. One would expect, therefore, a monatonic increase in k_d/k_c with increasing viscosity. The rate ratio, k_d/k_c, for reactions run in solvents ranging in viscosity between 0.48 and 2.68 cP (30 °C) is found to vary almost linearly with viscosity (see Figure 2). The k_d/k_c values in viscous, hydroxylic media, e.g., a 1:2 mixture of *tert*-butyl alcohol:pinacol (η 22.6 cP at 30 °C) were anomalously low, and can be attributed to the nonlinear relationship observed between macroscopic viscosity and the motion of the small *tert*-butyl radicals in alcoholic solvents.[4,5]



$$R\cdot + R\cdot \longrightarrow \overline{2R\cdot} \begin{cases} \xrightarrow{k_d} R(+H) + R(-H) \} \; P_d \\ \xrightarrow{k_c} R{-}R \} \; P_c \end{cases}$$

Since the data for the reaction of encounter pairs of *tert*-butyl radicals were available from Fischer's work[4-6] and since that same work contains a model for treating the viscosity dependence of the self reactions, it was obvious that examination of our system provided an opportunity to compare the viscosity dependence of the behavior of encounter pairs with that of geminately formed radical pairs.

Results

Products of the Reaction of AIB. Material Balance. Solutions of AIB (0.1 M) and thiophenol (0.5 M) in solvents of varying viscosity were photolyzed to 100% completion. Analyses of the products obtained from the photodecomposition are listed in Table I. The organic products, isobutane, isobutylene, 2,2,3,3-tetramethylbutane, and phenyl isobutyl sulfide, accounted for 96–100% of the theoretical quantity of *tert*-butyl radicals produced. The

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(1) D. D. Tanner, P. W. Samal, T. C.-S. Ruo, and R. Henruquez, *J. Am. Chem. Soc.*, **101**, 1168 (1979).

(2) Noyes' model for the reactions of geminate radical pairs predicts the relationship between cage efficiency and fluidity,[3] and a number of studies of this relationship have supported the model for the range of viscosities examined in ref 1. For a more detailed discussion see: T. Koenig and H. Fischer in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, 1973.

(3) R. M. Noyes, *Prog. React. Kinet.*, **1**, 129 (1961).

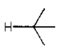
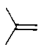
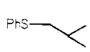
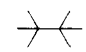
(4) H. Schuh and H. Fischer, *Helv. Chim. Acta*, **61**, 2463 (1978).

(5) H. H. Schuh and H. Fischer, *Helv. Chim. Acta*, **61**, 2130 (1978).

(6) B. Blank, A. Henne, and H. Fischer, *Helv. Chim. Acta*, **57**, 920 (1974).

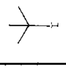
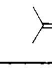
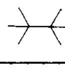
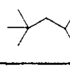
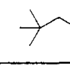
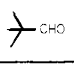
0002-7863/82/1504-0225$01.25/0

Table I. Photodecomposition Products of 2,2'-Azoisobutane (0.1 M) in a Variety of Solvents (30 °C) Containing (0.5 M) Thiophenol

point	solvent	η^a	product, N_2 mmol × 10^2	product, mmol/mmol N_2 × 10^2				$k_d/k_c{}^b$	cage yield,^{b} %
									
1	n-C_7H_{16}	0.384	22.2	137.1		38.9	8.45	4.58 ± 0.01	47 ± 0.0
2	C_6H_6	0.587	19.6	137.4	9.6	36.6	9.10	5.06 ± 0.02	56 ± 0.5
3	C_6H_5Cl	0.713	21.8	123.3	14.2	37.6	9.55	5.34 ± 0.06	59 ± 1.8
4	C_6H_5CN	1.13	22.0	123.9	37.1	22.0	9.40	6.25 ± 0.03	68 ± 0.0
5	n-$C_{14}H_{30}$	1.81^d	20.8	113.2	21.1	39.2	9.87	5.86 ± 0.25	70 ± 0.1
6	$(C_6H_5)_2O$	3.07	21.7	108.2	21.4	48.5	9.48	7.21 ± 0.15	79 ± 0.5
7	Nujol (L)^c	12.6	20.7	99.4	10.0	61.5	10.87	6.74 ± 0.16	80 ± 2.2
8	$(CH_3)_3COH/((CH_3)_2COH)_2$ (1/2)	16.6	20.8	96.8	72.6	4.8	10.77	6.98 ± 0.21	88 ± 0.1
9	Nujol (L/H), (1/1)	21.1	20.4	104.3	16.8	55.3	10.27	6.90 ± 0.12	81 ± 1.2
10	Nujol (L/H), (1/4)	32.9	21.0	99.9	20.2	51.0	10.57	7.06 ± 0.22	82 ± 1.7
11	Nujol (H)	48.6	21.0	99.6	33.1	45.5	8.74	8.18 ± 0.41	87 ± 1.0
12	Fluorolub oil	808	16.7	110.6	15.8	53.6	5.44	12.8 ± 0.01	77 ± 2.0
13	$(CH_3)_3COH/((CH_3)_2COH)_2$ (1/2)^e	27.6	20.2	87.2	80.4		10.45	7.27 ± 0.42	

[a] Viscosity, cP, of the solvent, containing 0.5 M thiophenol (30 °C). [b] Average values obtained from duplicate reactions. [c] Nujol (L), light paraffin oil; Nujol (H), heavy paraffin oil; Nujol (L/H) mixture of heavy and light paraffin oil. [d] Thiol concentration 0.112 M. [e] Reactions run without added thiol. Estimated, >80% cage reaction based on values obtained for reactions run in solvents of comparable viscosity.

Table II. Products and Relative Product Ratios for the Photolysis of Di-*tert*-butyl Ketone

expt	solvent^a	mmol CO × 1000	products, mmol/mmol of CO × 100					
								
1	$C_{12}H_{26}$	28.5	85.7	74.8	13.5	1.5	2.9	3.7
2	$C_{12}H_{26}$	28.7	86.2	75.1	13.2	1.3	3.2	3.0
			relative product ratios					
3	light Nujol, L		1	0.961	0.117	0.061	0.108	0.190
4	light Nujol, L		1	0.863	0.096	0.030	0.075	0.167
5	1:1 L/H		1	1.001	0.110	0.057	0.123	0.302
6	1:1 L/H		1	0.951	0.087	0.041	0.125	0.197
7	1:1 L/H		1	0.950	0.092	0.044	0.100	0.220
8	1:4 L/H		1	0.901	0.057	0.045	0.089	0.254
9	1:4 L/H		1	0.845	0.036	0.015	0.060	0.257

[a] Light Nujol, L; light/heavy Nujol, L/H.

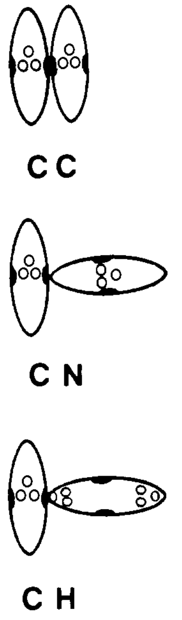


Figure 1. Pair configurations of colliding *tert*-butyl radicals. Black areas are reactive sites on the trivalent carbon. Open circles are the methyl hydrogens. Other bounded areas represent nonreactive sites.

Table III. Relative Termination Rate Constants for the Photodecomposition Reactions of Di-*tert*-butyl Ketone in Solvents of Viscosity η

experiment		η, cP	$k_d/k_c{}^b$	k_d/k_c
1	L	18.3	8.9	8.9 ± 0.1
2	L	18.3	9.0	
3	1:1 L/H	32.8	8.9	10.2 ± 0.9
4	1:1 L/H	32.8	11.6	
5	1:1 L/H	32.8	10.3	
6	1:4 L/H	49.4	14.9	17.2 ± 2.3
7	1:4 L/H	49.4	19.5	

[a] L/H, light:heavy paraffin oil; L, light paraffin oil. [b] Calculated as $[(CH_3)_2CCH_2 + (CH_3)_3CCH_2CH(CH_3)_2 + (CH_3)_3CCH_2C(CH_3)CH_2 - (CH_3)_3CCHO]/(CH_3)_3CC(CH_3)_3$.

percentage decomposition was based on the nitrogen collected (see Table I).

Photodecomposition of Di-*tert*-butyl Ketone. Solutions of di-*tert*-butyl ketone (3 vol %) in solvents of viscosities ranging from 1.18 to 49.4 cP were photolyzed for an estimated 3 to 5% completion based on the carbon monoxide evolved in typical reactions (see Table II). Analyses of the products obtained from the photodecompositions are listed in Table II. The organic products accounted for 99–100% of the theoretical quantity of *tert*-butyl radicals that were produced (see Table II). The products resulting from the reactions of the *tert*-butyl radicals were isobutane, isobutylene, 2,2,3,3-tetramethylbutane, 2,4,4-trimethylpentane, pivalaldehyde, and 2,4,4-trimethyl-1-pentene.

In order to substantiate that in the very highly viscous solvents the coupling and disproportionation products were still formed solely from encounter pairs, the photodecompositions were also carried out in a 4:1 mixture of heavy:light Nujol with an added scavenger (η = 35.7, 30 °C), carbon tetrachloride (0.5 M). The analysis of the products resulting from these reactions showed them to be besides carbon monoxide the following: *tert*-butyl chloride, hexachloroethane, chloroform, and traces of pivalaldehyde and isobutylene.

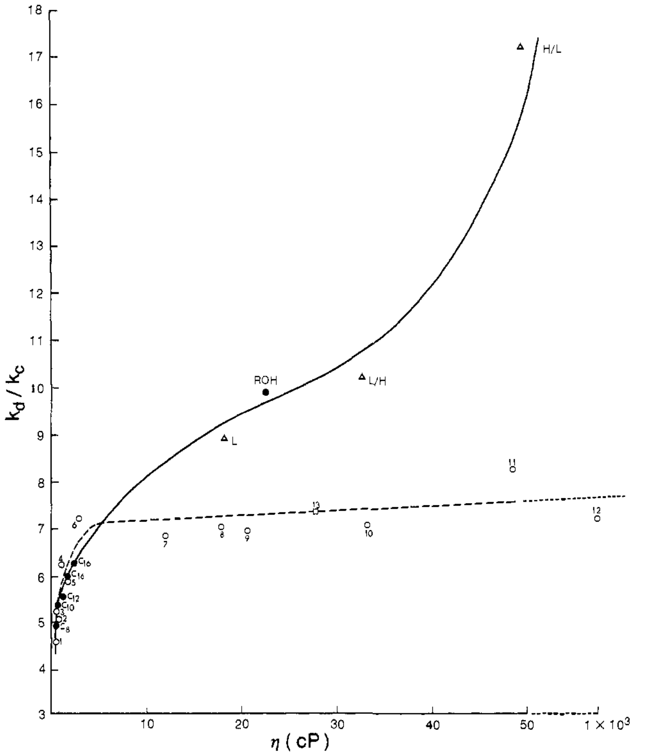


Figure 2. Plot of the ratio of cage disproportionation to combination rate constant, k_d/k_c, as a function of solvent viscosity, η. The open symbols (○, □), correspond to the points listed in Table I for the photodecomposition of 2,2′-azoisobutane. The closed circules (●), are the values taken from ref 4 (extrapolated to 30 °C) and were obtained from analyses of the photodecomposition products of di-*tert*-butyl ketone in the solvents listed: C_8, *n*-octane; C_{10}, *n*-decane; C_{12}, *n*-dodecane; C_{14}, *n*-tetradecane; C_{16}, *n*-hexadecane; ROH, (1/2) $(CH_3)_3COH/((CH_3)_2COH)_2$. The triangles (△) are for the photolysis of di-*tert*-butyl ketone in solvents: light Nujol (L), a 1:4 mixture of light:heavy Nujol (L/H), and in a 4:1 mixture of heavy:light Nujol (H/L).

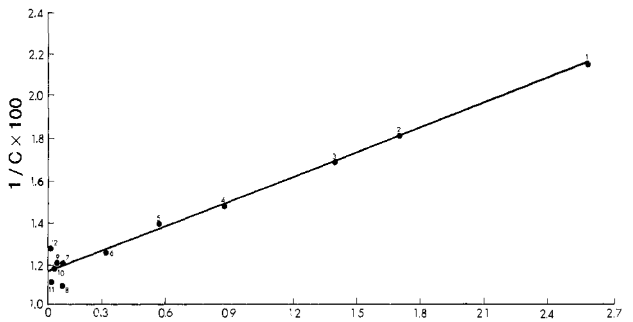


Figure 3. Plot of the fluidity, $1/\eta$, of the solvent used vs. the cage efficiency, $1/c$, for the formation of the cage products during the photodecomposition of 2,2′-azoisobutane. Numbers correspond to the solvents listed in Table I.

Viscosity Measurements. The viscosities of the solvent reported (see Table I) were measured at 30 °C with added thiophenol (0.5 M) and those reported in Table III were measured at 30 °C with 3 vol % of added di-*tert*-butyl ketone. The addition of solute to the solvents used, especially those of high viscosity, made large changes in the observed bulk viscosities.

Discussion

Photodecomposition of Di-*tert*-butyl Ketone. In order to make a more extensive compairson between the reactions of geminate and encounter pairs, the range of viscosities covered by the study of the encounter reactions was extended from dodecane (k_d/k_c = 5.6, ref 4, k_d/k_c = 5.7, this work), η = 1.18 cP, to a solvent mixture of 1:4 light/heavy Nujol, η = 49.4 cP (see Table II). The observed increase in the k_d/k_c values with increasing viscosity of the media, over the extended range of viscosity (see Table III and Figure 2, solid line), lends qualitative support to the validity of the collision model; however, the expected linearity of the correlation was not substantiated.

The possibility did exist that when very high viscosity solvents were used as the media for the photodecomposition reactions of the ketone, translational diffusion times would be increased to a point that they would be competitive with decarbonylation. If this occurred then self combination and self disproportionation could, likewise, occur in the solvent cage. The occurrence of cage reactions due to this process could, however, be ruled out since when the photolysis of the ketone was carried out in a mixture of 4:1 heavy:light Nujol with an added scavenger (η = 35.7, 30 °C), carbon tetrachloride (0.5 M), no combination, 2,2,3,3-tetramethylbutane, nor disproportionation, isobutane, products were detected.

The rationalization used by Fischer to explain the deviation from linearity of the experimental ratios obtained for the reactions carried out in hydroxylic solvents may be correct; however, the value of k_d/k_c obtained in the alcoholic solvent (*tert*-butyl alcohol/pinacol, see Figure 2, point ROH) does not appear to differ greatly from those obtained in the highly viscous nonhydroxylic solvents. The macroviscosity of the solvent reflects the interaction of the solvent molecules with molecules of their own kind, and for long-chain molecules may involve chain tangling, while the rotation of small molecules in these solvents are subject to local or micro environments which may have significantly different local viscosities.[7,8] Likewise, the addition of additives, di-*tert*-butyl ketone, greatly affects the bulk viscosity of the solvent, but may have little effect on the microviscosity encountered by small molecules. Since only a limited understanding of the effects of microviscosity on molecular motion exists, it is not suprising that the linear relationship predicted for the collision model does not hold for such a wide range of solvents. It is, however, in agreement with the model that in all cases the higher the macroviscosity of the solvent the higher is the observed ratio of the termination rate constants, k_d/k_c.

Differentiation between Encounger and Geminate Pair Reactions. The model should also be capable of treating the behavior of geminately formed radical pairs if rotational and vibrational relaxation times are shorter than the lifetimes of the radical pairs, since only differences that should be capable of leading to different reactivity patterns between cage and encounter pairs are those which involve initial rotational and vibrational relaxation, statistical spin multiplicity corrections, and factors involving the intervening molecules (e.g., nitrogen). Possible variations between the behavior of encounter and geminate radical pairs have been discussed in terms of factors which are directly related to the above considerations.[9]

Differences in the ratios of combination/disproportionation associated with the spin multiplicity of the radical pairs have not been observed.[10] However, encounter pairs have a statistical distribution of spin orientations (one in four combinations are singlets), the majority of which (the triplet pairs) do not lead to combination reactions; disproportionation reactions are equally inhibited.[5]

Kochi[11] has concluded that the relative self-termination rates are the same for radical pairs reacting in a solvent cage or from the encounter of two free radicals. This conclusion was based on a lack of change in k_d/k_c for a number of alkyl radicals generated via photolysis of diacyl peroxides in solvents which promote varying amounts of cage reaction. These observations, presumably, preclude any detectable effect from the intervening carbon monoxide molecules.

In solution-phase reactions, unlike the reactions in the vapor phase, no evidence could be obtained for the effect of vibrational

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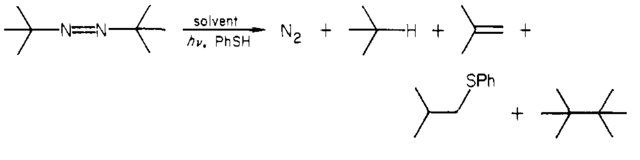
(7) A. North, *Q. Rev., Chem. Soc.*, **20**, 421 (1966).
(8) L. F. Meadows and R. M. Noyes, *J. Am. Chem. Soc.*, **82**, 1868 (1960).
(9) M. J. Gibian and R. C. Corley, *Chem. Rev.*, **73**, 444 (1973).
(10) P. S. Engel and P. D. Bartlett, *J. Am. Chem. Soc.*, **92**, 5883 (1970).
(11) R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **92**, 4395 (1970).

excitation on the reaction ratios, k_d/k_c, of radical pairs.[11,12]

The rotational relaxation times of relatively large radicals have been shown to be large enough that termination reactions could show differences in behavior between geminate and encounter pairs. Thus, both Greene[13] and Kopecky,[14] independently studying the decomposition of optically active azo compounds, showed that while the k_d/k_c ratios for two α-phenylethyl radicals or an α-phenylethyl radical plus a benzyl radical are the same for caged and encounter pairs, recombination of a geminate pair is only about 14 times slower than rotation of one of the radicals with respect to the other. They reached this conclusion since some residual activity remained in the recovered coupling products. This observation predicts that both cage and encounger pairs can differ in products if the productforming reactions themselves are dependent on molecular rotation. This appears to be the case for reactions carried out in the solid state where Bartlett[15] and McBride[16] have both observed large differences in k_d/k_c from reactions run in a solid matrix where rotational motions are relatively restricted.

Caged Radicals Produced from the Decomposition of 2,2′-Azoisobutane. The photodecomposition (30 °C) and analysis of the reaction products from photolysis of 2,2′-azoisobutane (0.1 M) were carried out as previously reported[1] except that the range of viscosities studied was extended, thiophenol was used in place of its deuterated analog, and the substrates (solvents) used were even less reactive toward abstraction by *tert*-butyl radicals than the toluenes that were previously used (see Table I). Under the reaction conditions previously reported (0.1–3 M deuteriothiophenol),[1] all of the cage escape radicals reacted by hydrogen or deuterium abstraction with either thiophenol-*d*, thiophenol (residual protiated thiol from incomplete deuteration), or solvent toluene.[17] In this study the concentration of thiol chosen, 0.5 M, was kept well within the concentration range previously reported to eliminate a detectable amount of disproportionation or combination external to the solvent cage, and since the deuterium isotope effect has been estimated[1] as $k_H/k_D \approx 5$; the conditions reported in this report, 0.5 M protiated thiophenol, assure the complete scavenging of the cage escape radicals.



As previously observed a linear relationship between the fluidity of the solvent, $1/\eta$, and the cage efficiency, $1/c$, of the radicals was obtained over the range of viscosities covered by the study carried out in solvent toluenes (0.5–3.5 cP); however, at very high viscosities (12.6–808 cP) some deviation from thhis behavior is observed; see Figure 3.

The linearity of the plot over the viscosity range 0.38–12.6 cP is consistent with our previous report over the more truncated range available by limiting the study to a series of substituted toluenes. The observation is inconsistent with the recent statement by Pryor et al.[18] which reports that the yield of olefin, obtained from the decomposition of AIB in a series of *n*-alkanes (used as solvents), was constant over a viscosity range of 0.8–1.8 cP. Whether termination, in that report, is due to cage or encounter pair reactions, the observation is inconsistent with the increasing values of olefin reported by Fischer for encounter pair reactions[4] or in this work for the disproportionation reactions of caged pairs (see Table I). As is seen below, at these ranges of viscosity both encounter and cage pairs show the same disproportionation behavior. Since no experimental data were provided in this abstract[18] it is inappropriate, at this time, to comment on the report.

The deviation of the plot of cage efficiency, $1/c$, vs. fluidity at very high viscosities (16.6–808 cP) is expected, since translational diffusion, like rotational, is not directly related to macroviscosity for small molecules in solvents of long-chained hydrocarbons.[7,8,19]

Comparison of Encounter and Geminate Pair Reactions of *tert*-Butyl Radicals. A compairson between the effect of viscosity upon the disproportionation–combination ratios observed for encounter pairs and geminate pairs is seen in Figure 2. The viscosity dependence of the k_d/k_c ratios (both η and k_d/k_c extrapolated to 30 °C) reported by Fischer[4] from an analysis of the products obtained from the reaction of encounter pairs for solvent viscosities over the range 0.48–2.67 cP is almost identical with those obtained in this study of the reaction of geminate pairs (see Figure 2). The similarity of values obtained at low viscosities suggests that the *tert*-butyl radical pairs generated from the azo photolysis are formed with sufficient rotational energy to appear to be randomly oriented. The products from the reaction of these geminate pairs are controlled, as are the products from the encounter pairs, by anisotropic reorientation.

At viscosities larger than 3 cP the ratios of termination rate constants for the encounter and geminate pair reactions are seen to diverge (see Figure 2). Although at higher viscosities the values observed for the reaction of encounter pairs are not linearly related to the macroviscosity of the media, the observed values of k_d/k_c are always significantly larger than those obtained for the geminate pair reactions. Over the range of viscosities from 12–808 cP the ratio of termination constants for the geminate pairs does not increase significantly (Figure 2, points 7–12), and it appears that the free reorientational model fails to predict the value of k_d/k_c. The kinetic behavior of the geminate pairs in the very viscous solvents suggests that a random array of collisional orientations is not available to the radical pairs at birth. The nonrandom orientation of the radicals upon formation appears to be more biased toward a relatively larger amount of combination in opposition to the effect of viscosity on reorientation.

The stereochemistry of the photodecomposition of azo-*tert*-butane[20] may have some bearing upon the orientational preference for reaction of the caged pair of *tert*-butyl radicals. Azo-*tert*-butane as obtained from synthesis has the trans configuration.[20] Upon irradiation the trans-azo compound undergoes trans-cis isomerization.[20a] The cis isomer, however, thermally decomposes rapidly at temperatures higher than 0 °C. Under the reaction conditions used in the present study ($h\nu$ irradiation at λ >310 nm, 30 °C) trans to cis interconversion is the primary photochemical reaction. Accompanying the isomerization an efficient thermal decomposition of the cis isomer takes place at ambient temperatures. Reaction of these cis-born radical pairs in viscous media appears to be biased toward combination and presumably rotational diffusion times have been increased in the highly viscous

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(12) (a) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 143 (1966). (b) H. P. Watts and G. S. Hammond, *ibid.*, **86**, 1911 (1964). (c) P. S. Dixon, A. P. Stefani, and M. Szwarc, *ibid.*, **85**, 2551 (1963).

(13) F. D. Greene, M. Berwick, and J. C. Stowell, *J. Am. Chem. Soc.*, **92**, 867 (1970).

(14) K. R. Kopecky and T. Gillan, *Can. J. Chem.*, **47**, 237 (1969).

(15) S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 137 (1966).

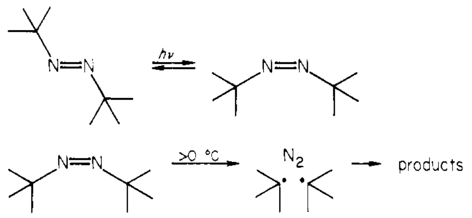
(16) (a) J. M. McBride, *J. Am. Chem. Soc.*, **93**, 6302 (1971). (b) A. B. Jaffe, K. J. Skinner, and J. M. McBride, *ibid.*, **94**, 8510 (1972).

(17) When the azo decomposition was carried out in neat toluene the disproportionation and combination products accounted for 85% of the products identified; however, only 89% of the *tert*-butyl radicals were accounted for.[1] One of the (>7) minor products (2.7%) formed was identified as *tert*-butyl toluene. It was subsequently pointed out (unpublished work) by both Dr. D. C. Nonhebel and Dr. W. A. Pryor that the structure of this material was misassigned (GLC retention time and mass spectral cracking pattern). The reaction product has now been identified (GLC retention time and GC/MS cracking pattern, 10 m × 0.25 mm i.d. glass WCOT Sp 2100 column, 40 °C) as a mixture of four products—neopentylbenzene and tentatively (GLC retention time) *o*- and *p*-*tert*-butyltoluene and an unidentified compound formed in an approximate 11:1:1:1 mixture. The GC/MS of the original mixture (the shoulder of the GC peak) was consistent with *o*- and *p*-*tert*-butyltoluene, and this observation presumably accounted for the original identification.

(18) W. A. Pryor, R. H. Tang, F. Y. Tang, and D. F. Church, Abstracts, 181st National Meeting of the American Chemical Society, Atlanta, Georgia, March 1981, Orgn 96.

(19) N. E. Hill, *Proc. Phys. Soc., London, Sect. B*, **67**, 149 (1954); ibid., **68**, 209 (1955).

(20) (a) T. Mill and R. S. Stringham, Tetrahedron *Lett.*, 1853 (1969). (b) P. S. Engel and D. J. Bishop, *J. Am. Chem. Soc.*, **97**, 6754 (1975).



solvents to the point where differentiation between different competing reactions (combination–disproportionation) is observed.

Experimental Section

Materials. All solvents were purified before use. *n*-Heptane (MC&B Co.) and tetradecane (Aldrich Chemical Co.) were washed several times in succession with concentrated sulfuric acid, 10% aqueous sodium carbonate, and distilled water. The solvents were dried over anhydrous magnesium sulfate and fractionally distilled. GLC analysis (20 ft × $^1/_8$ in. 10% QF-1 on 80–100 Chromosorb W AW DMCS, glass column) showed them to be >99.5% pure. Chlorobenzene (Aldrich Chemical Co.) was fractionally distilled, and shown by GLC (QF-1 column) to be >99.9% pure. Benzonitrile (BDH), benzene (Fischer Scientific Co.) and diphenyl ether were purified by repeated low-temperature fractional recrystallization, fractionally distilled and checked for purity, >99.8% by GLC (QF-1 column).

The paraffin oils (MC&B and BDH) were dissolved in purified dodecane and washed with concentrated sulfuric acid until no discoloration was noticeable. After separation of the organic layer, the hydrocarbon solution was washed successively with water, 10% sodium carbonate, and water and dried over anhydrous magnesium sulfate and alumina, and dodecane was removed under vacuum. Fluorolube oil was heated to 180 °C at 0.5 (mmHg) for 48 h and used without further purification. *tert*-Butyl alcohol (Fisher Scientific Co.) and Pinacol (Fluka) were fractionally distilled and checked for purity by GLC (20 ft. × $^1/_8$ in. 10% Carbowax 20 M on 60–80 mesh Chromosorb W AW DMCS, glass column); they were found to be >99.9% pure. Thiophenol (Aldrich Chemical Co.) was fractionally distilled and shown to be >99.5% pure by GLC (Carbowax Column). Isobutane, isobutylene, and 2,2,3,3-tetramethylbutane (Aldrich Chemical Co.) were used without further purification. AIB was prepared by the method of Stowell.[21] The azo compound was fractionally distilled using a 24-in. Teflon spinning band column. AIB [bp. 106–107 °C (690 mmHg); NMR (CDCl$_3$) δ 1.15 (s, C(CH$_3$)$_3$); UV (C$_6$H$_6$) λ_{max} 370 nm (ϵ 26)] (lit. bp 98–109 °C,[21] 109–110 °C[22]); GLC analysis (Carbowax column) showed this compound to be >99.5% pure.

Isobutyl phenyl sulfide was prepared according to the method of Ipatieff:[23] isobutyl phenyl sulfide [bp. 100–102 °C (11 mmHg); NMR (CDCl$_3$) δ 1.01 (d, 6 H, J = 5.96 Hz, CH$_3$), 1.86 (m, 1 H, H-2), 2.79 (d, 2 H, J = 1.70 Hz, CH$_2$), 7.3 (m, 5 H, aromatic)].

Di-*tert*-butyl ketone (CPL) was fractionally distilled, bp 140 °C (700 mmHg), [lit.[24] bp 154 °C (740 mmHg)], and was shown to be >99.5% pure by GLC analysis (Carbowax column).

Photodecomposition of AIB in the Presence of PhSH. Mixtures of AIB (~0.1 M) and thiophenol (0.5 M) were dissolved in the appropriate solvent. An aliquot of the solution was transferred to a Pyrex reaction vessel, degassed, and sealed. The portion of the vessel above the liquid was covered with foil, and the vessel was placed into a Rayonet photochemical reactor (3500 Å BL lamps) equipped with a merry-go-round and irradiated for 14 h (30 °C). The reaction vessel was connected to a vacuum line, frozen (−198 °C), and opened. The noncondensable gases were measured using a Toepler pump. A sample of the gas collected was subjected to mass spectral analysis and was shown to be solely N$_2$. The solution remaining in the reaction vessel was distilled through two −78 °C traps (for the reactions carried out in *n*-Heptane, −110 °C traps were used) into a trap at −198 °C, and the condensable gases C$_4$H$_{10}$ and C$_4$H$_8$ were collected. For the reactions which were carried out in highly viscous solvents such as Nujol, it was necessary to warm up the reaction vessel to ~50 °C to make sure that all the isobutane and isobutylene had been distilled. The total amount of condensable gas was measured in the Toepler pump, and their relative amounts were determined by vaccum line GLC using a Gow Mac TR-TH thermal conductivity GLC fitted with a 10 ft. × $^1/_4$ in. 10% silicone oil 200 on 60/80 Chromosorb W AW glass column, 0 °C. The residual reaction mixture was transferred back into the reaction vessel and removed from the vacuum line. A weighed amount of standard (undecane, dodecane, or hexadecane) was added to the mixture and the mixture was subjected to GLC analysis (Carbowax or QF-1 columns).

The remaining products, 2,2,3,3-tetramethylbutane and phenyl isobutyl sulfide, were identified by their mass spectral cracking pattern and their GLC retention times compared with those of authentic samples. The results of a representative number of these analyses are listed in Table I.

Photolysis of Di-*tert*-butyl Ketone. Aliquotes of solutions of di-*tert*-butyl ketone (3 vol %) in the appropriate solvent were degassed and sealed in Pyrex reaction tubes fitted with break-seals. The protion of the vessel above the liquid was covered with foil and the reaction mixtures were photolyzed in a Rayonet reactor (2530-Å lamps), equipped with a merry-go-round, at 30 °C for 0.5 h. Repeated analysis of the reaction mixtures, based on CO evolved, showed that the photolysis had proceeded from 3–5% under these conditions. The product mixtures were analyzed by either opening the reaction vessels to the vacuum line and measuring the CO (as described above for the nitrogen analysis) or by injecting, upon first melting, the cooled (−80 °C) reaction mixture directly into the GLC column (20 ft. × $^1/_8$ in. *n*-octane/proasil C, 100–120 mesh glass column). The method was calibrated by analyzing the synthetic mixture of the products and the analysis was shown to have the same reproducibility as that found for analysis of duplicate reaction mixtures. For the reactions carried out in dodecane an internal standard, *n*-nonane, was added to obtain the absolute amounts of the products.

Viscosity Measurements. The viscosities of all the solvent mixtures reported in this work were determined at 30 °C using an Ostwald viscometer, calibrated using distilled water as standard.[25]

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Registry No. AIB, 927-83-3; di-*tert*-butyl ketone, 815-24-7; thiophenol, 108-98-5.

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(21) J. C. Stowell, *J. Org. Chem.*, **32**, 2360 (1967).

(22) E. Farenhorst and E. C. Kooyman, Recl. *Trav. Chim. Pays*-Bas, **72**, 993 (1953).

(23) V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Am. Chem. Soc.*, **60**, 2731 (1938).

(24) F. C. Whitmore and E. E. Stahly, *J. Am. Chem. Soc.*, **55**, 4153 (1933).

(25) F. Daniels, J. W. Williams, P. Bender, R. A. Alberty, C. D. Cornwell, and J. E. Harriman, "Experimental Physical Chemistry", 7th ed., McGraw-Hill, New York, 1978, p 164.