Polar Radicals. 12.[1] A Reinvestigation and Reappraisal of the Apparent Polar Effects Observed during the Reactions of *tert*-Butyl Radicals. Decomposition of 2,2′-Azoisobutane and *tert*-Butyl Perpivalate in Substituted Toluenes

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Abstract: The photodecomposition of 2,2′-azoisobutane (0.1 M), in solutions of toluene or a substituted toluene, with added thiophenol-*d* (0.1–3 M) yielded isobutane, 2-deuterioisobutane, isobutylene, phenyl 2-deuterioisobutyl sulfide, and nitrogen. A material balance based on *tert*-butyl radicals produced showed that very little, if any, of the isobutane formed was the product of an abstraction reaction from the solvent toluene. The isobutane instead was formed primarily from a cage disproportionation reaction. The relative rates of formation of isobutane and the isobutane-*2-d* produced by abstraction from thiophenol-*d* (0.7 or 3 M) varied in a uniform manner from substrate to substrate and the values of their relative rate constants gave an excellent Hammett correlation, when *m*- and *p*-phenoxytoluene were not included. As reported previously a positive ρ was obtained. However, the correlation can also be interpreted as being due to the effect of the viscosity of the substrate (solvent) toluene, since a plot of the log (relative viscosity) of the substrate toluenes showed a good Hammett correlation with their σ substituent constants, again excluding the highly viscous *m*- and *p*-phenoxytoluenes. This ρ value was positive and the same as that obtained in the decomposition reactions ($\rho = +0.6$). Moreover an excellent linear correlation was obtained from a plot of the relative rates of formation of the deuterated and protiated isobutane vs. the fluidity ($1/\eta$) of all of the solvents. The importance of cage disproportionation was further substantiated and the anomalous behavior of the phenoxytoluenes was explained since a plot of the cage efficiency (1/olefin yield) vs. the fluidity of the solvent ($1/\eta$) gave a linear correlation, $r = 0.97$, for all of the substrates. An alternative source of *tert*-butyl radicals was produced from the photodecomposition (30°C) and thermal decomposition (55°C) of solutions of *tert*-butyl perpivalate in the same substrates. The *tert*-butyl radicals from these decompositions formed isobutane, exclusive of disproportionation. The relative rate constants for isobutane formation from these reactions did not give a satisfactory Hammett correlation since as in the case of the azo decomposition only a negligible amount of abstraction had taken place.

Since the early suggestions that polar effects could explain certain structure–reactivity relationships found in free-radical reactions,[3] a large number of radical reactions have been shown to give a correlation with the Hammett equation. These linear free energy correlations have usually been interpreted as being due to the effect of the structural changes on a polar transition state.[4]

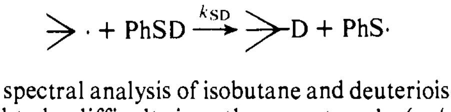
Several years ago Zavitsas and Pinto[5] put forward an alternative suggestion that the effects of polar substituents on transition-state stabilities were unnecessary considerations in rationalizing the relative rates of hydrogen transfer reactions of free radicals with substituted toluenes. They proposed instead that the effects observed could be adequately explained on the basis of the changes effected by the substituents on the bond dissociation energy (BDE) of the benzylic C–H bond. As a consequence of this suggestion, if BDEs controlled the reactivity of a series of reactions, then all radicals, regardless of their polarity, should exhibit the same order of reactivity. Since most of the radical reactions that had been studied were accelerated by electron donation, the proposal suggests that all benzylic abstraction reactions should exhibit negative ρ values. In opposition to this suggestion a number of studies of the abstraction reactions of nucleophilic alkyl radicals from substituted toluenes were subsequently reported. The alkyl radicals *tert*-butyl,[6,7] isopropyl,[7] undecyl,[8,9] and 1-ethylpentyl[10] all were reported to have positive ρ values.

The reactivity of a relatively unselective carbon-centered radical, not attached to a highly electronegative atom, i.e., a phenyl or methyl radical, would show little or no correlation to substituents and would be predicted to have a ρ value of zero or nearly so. In agreement with this prediction the ρ value found by Russell for phenyl radical abstraction[11] was −0.1, and that found by Pryor for methyl[12] was -0.2 ± 0.2.

In light of these predictions the high positive values reported for hydrocarbon radicals (undecyl,[8,9] +0.5; isopropyl,[7] +0.8; 1-ethylpentyl,[10] +0.7; *tert*-butyl,[6,7] 1.0) are surprising since their reactions should be quite exothermic and unselective ($-\Delta H \simeq 6$–13 kcal/mol) and their difference in electronegativity compared to the benzyl carbon should be rather small.

In the course of our study on the decomposition of *tert*-butyl peroxypivalate (BPP) and its substituted homologues[13,14] we had interest in investigating the fate of *tert*-butyl radicals in aromatic solvents. Germane to this interest was the study by Pryor on the reactivity of *tert*-butyl radicals with substituted toluenes. The method used by these authors to obtain the relative selectivities for abstraction of the benzylic hydrogen by *tert*-butyl radicals from their series of substituted toluenes was a competitive one. Mixtures of a chosen toluene and deuteriothiophenol or *tert*-butyl mercaptan-*d* were used as solvent in which to carry out the photochemical decomposition of 2,2′-azoisobutane (AIB) or BPP.

The *tert*-butyl radicals produced in the photolysis were presumed to competitively abstract either a deuterium from the thiol (k_{SD}) or a protium from the benzylic position of the toluene (k_a). Mass spectral analysis of the ratio of isobutane and isobutane-*2-d* formed in the reaction was related to the relative rates of abstraction.



The mass spectral analysis of isobutane and deuterioisobutane was found to be difficult since the parent peaks (*m/e* 58 and 59) were found to be too small to measure, and instead the intensities of the P − 15 peaks (*m/e* 43 and 44) were used to

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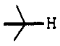
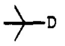
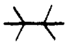
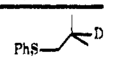
Table I. Photodecomposition of AIB

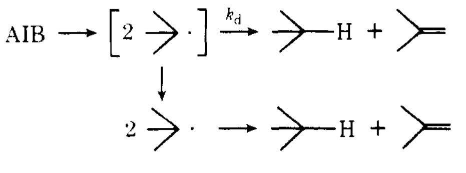
substrate $ArCH_3$	starting material, mol/L × 10^2			products, mol/mol AIB (10^2) N_2	products, mol/mol N_2 (10^2)					uncor max[a] abstraction from $ArCH_3$, %	cor max[b,d,e,f] abstraction from $ArCH_3$ %
	[AIB]	$[C_6H_5SD]$	$[ArCH_3]$								
$C_6H_5CH_3$	10.2	61.4	853.3	99.5	73.5	48.0	13.7	9.80	31.4	28.4	8.2
$C_6H_5CH_3$	10.2	309	606.8	100	66.8	54.3	18.3	9.13	28.4	20.1	0.0 (−2.7)
p-$ClC_6H_4CH_3$	10.5	75.7	735.5	92.4	72.2	46.4	29.4	7.7	28.9	13.9	2.8[c]
p-$ClC_6H_4CH_3$	10.3	297	567.6	82.4	71.1	52.6	25.4	8.7	32.4	13.3	0.68[c]
p-$CNC_6H_4CH_3$	10.1	64.9	729.2	100.4	82.7	36.0	37.5	10.9	21.6	23.6	16.0[f]
p-$CNC_6H_4CH_3$	10.1	311.0	547.3	99.5	74.7	40.6	52.0	9.4	11.4	11.3	1.6[c]
m-$ClC_6H_4CH_3$	10.3	85.3	727.3	83.0	73.1	44.4	42.7	10.5	14.0	16.4	0.0 (−2.2)
p-$MeC_6H_4CH_3$	10.4	66.0	734.2	100	76.0	48.6	37.0	8.7	14.9	24.1	3.7
p-$MeC_6H_4CH_3$	10.6	322	524.8	98.1	69.7	55.8	37.5	9.1	18.3	13.9	0.51[c]
m-$MeC_6H_4CH_3$	10.2	84.8	756.4	98.6	77.8	46.1	21.8	10.4	26.8	29.2	9.8
p-$C_6H_5OC_6H_4CH_3$	10.4	69.1	509.3	97.5	84.7	27.1	36.4	8.1	35.2	13.1	7.4[f]
p-$C_6H_5OC_6H_4CH_3$	10.3	69.7	514.7	100.0	87.3	26.9	40.2	7.6	31.8	15.3	9.6[f]
m-$C_6H_5OC_6H_4CH_3$	10.4	68.0	518.2	96.2	82.0	26.0	61.4	8.1	12.4	8.2	2.7[f]
m-$C_6H_5OC_6H_4CH_3$	10.1	62.3	523.9	99.9	78.7	26.7	52.1	8.9	21.1	5.5	0.0 (−0.1)[f]

[a] Calculated from ($[C_4H_{10}] - [C_4H_8] - [C_4H_9DSC_6H_5]$) = uncorrected maximum abstraction, i.e., abstraction by C_4H_9 not due to disproportionation. [b] Sample 2 of the thiophenol-*d* was used (except where indicated, footnote *c*). The corrections used were those for the appropriate sample; see Table II. [c] Sample 1 of the thiophenol-*d* was used in these reactions (see Table II). [d] Uncorrected maximum abstraction minus abstraction from thiophenol; see Table II. [e] Corrected maximum abstraction was calculated as $[C_4H_{10}]_{total} - [C_4H_9D]f$, where f is the ratio $f = \{[C_4H_{10}]_{total} - ([C_4H_8] + [C_6H_5S\text{-}C_4H_8D])\}/[C_4H_9D]$, found in the decomposition of AIB in mixtures of Freon and the sample of thiophenol-*d* used (see Table II). [f] Sample 3 of the thiophenol-*d* was used in these reactions (D_2O-saturated thiophenol-*d*).

determine these ratios. If one assumed that k_{SD} was constant for a series of reactions carried out using different substituted toluenes then the relative rates of abstraction from these toluenes have been determined as the ratio of any two individual reactions.

The major limitation inherent in the use of this kinetic analysis is the assumption that the benzylic hydrogen of the arylalkane was the only kinetically important source of protium available for the formation of isobutane. Upon a detailed analysis of this problem the authors considered the possibility of a number of other alternate transfer agents which could conceivably react with the *tert*-butyl radicals to form isobutane.[6,7] The arylation of the substrate toluene, the induced decomposition of the initiators AIB and BPP, the disproportionation reaction of a *tert*-butyl radical, and the abstraction of protium from thiophenol impurities in the thiophenol-*d* were considered as alternative sources of protium responsible for the formation of isobutane. The first two processes were reported not to occur; while there was evidence for the latter two, the authors argued that these reactions were negligible to their analysis.

It was recognized that isobutane may also be formed by disproportionation of the radicals produced from the decomposition of AIB and BPP both in the solvent cage and after escape from the cage; see eq 1. The latter mode of reaction was



(1)

easily ruled out in the case of AIB by the demonstration that the yield of combination product (2,2,3,3-tetramethylbutane), formed in a relatively constant ratio with its disproportionation products,[15,16] did not change with increasing thiol concentration. The low yield of combination product was used to set a limit (~5%) on the importance of cage disproportionation, since the disproportionation to combination ratio (~5) for *tert*-butyl radicals had previously been determined.[15] In the case of BPP the formation of isobutane by cage disproportionation does not occur[17] and it was assumed that, as in the case of the AIB decompositions, the high concentration of scavengers (toluene and thiophenol) would scavenge any radicals which escape from the cage prior to their disproportionation.

A constant fraction of the isobutane formed from the reactions of *tert*-butyl radicals will be due to the abstraction of protium from the small amount of impurity, thiophenol, in the deuterated mercaptan. The amount of this impurity could be limited by the use of thiophenol-*d* which was saturated with D_2O.[7] Since this ratio of H to D abstraction was constant in all of the relative reaction rates run, this complication does not affect the slope of the plot of the ratio of relative rate constants vs. substituent constants, but only its intercept.

The conclusions drawn from our reinvestigation of the photochemical decomposition of AIB and BPP in mixtures of thiophenol-*d* and toluenes are not in accord with those reached by the previous investigators,[6,7] since a reinvestigation of the reactions made it difficult to ignore the above assumption, that the only kinetically important source of protium in the system was a toluene or substituted toluene. It is to this point that we would like to direct this report and further to propose an alternate explanation for the previously reported, and herein reproduced, results.

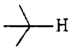
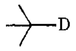
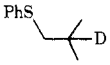
Results

Products of the Reactions of AIB. Material Balance. Solutions of AIB (0.1 M) and thiophenol-*d* (0.1–3 M) in a chosen toluene were photolyzed to from 82 to 100% completion. Analyses of the products obtained from the photodecomposition (0.7–3 M) are listed in Table I. The organic products accounted for from 87 to 100% of the theoretical quantity of *tert*-butyl radicals produced. The products resulting from the reactions of *tert*-butyl radicals were isobutane, isobutane-*2-d*, isobutylene, 2,2,3,3-tetramethylbutane, and phenyl isobutyl-*2-d* sulfide. The percentage of decomposition was based on the nitrogen collected (see Table I).

The decomposition of AIB (0.13 M) in solvent toluene without added thiophenol yielded, besides nitrogen (2.54 mmol, 98%), isobutane (1.97 mmol), isobutylene (1.48 mmol), 2,2,3,3-tetramethylbutane (0.44 mmol), and two new products: bibenzyl (0.043 mmol) and *tert*-butyltoluene (0.15 mmol). In addition to these products a number of minor products (>7) were detected (GLC); however, these were not identified. The products identified accounted for 89% of the *tert*-butyl radicals produced.

Isotopic Purity of Thiophenol-*d*. The amount of isobutane resulting from the abstraction of protium from thiophenol contained in the deuterated mercaptan was determined by an analysis of the products obtained from the photodecomposition of AIB (0.1 M) in a Freon 113 solution of the thiophenol-*d*

Table II. Photodecomposition of AIB in Freon 113

starting material, mol/L × 10^2		products, mol/mol AIB × 10^2 N$_2$	products, mol/mol N$_2$ × 10^2					material balance based on C$_4$H$_9$ radicals
[AIB]	[C_6H_5SD]							
10.0	314[a]	87.5	65.1	60.6	15.4	35.4	9.7	99.0%
10.1	311[b]	91.0	71.0	61.2	5.5	39.9	9.3	98.1%
10.3	62.4[c]	98.0	65.9	58.7	17.0	34.9	11.9	100.1%
10.3	295.6[c]	99.0	56.3	70.7		73.4	9.0	95.2%

[a] Sample 1 of thiophenol-*d* used in reactions listed in Table I. [b] Sample 2 of thiophenol-*d* used in reactions listed in Table I. [c] Sample 3 of thiophenol-*d* used in reactions listed in Table I.

Table III. Viscosity of a Number of Substituted Toluenes (30 °C)

ArCH$_3$	η^{30}, cP	ArCH$_3$	η^{30}, cP
$C_6H_5CH_3$	0.526[a]	*p*-$ClC_6H_4CH_3$	0.819
m-$MeC_6H_4CH_3$	0.572[a]	*p*-$BrC_6H_4CH_3$	1.104
p-$FC_6H_4CH_3$	0.589	*p*-$CNC_6H_4CH_3$	1.437[b]
p-$MeC_6H_4CH_3$	0.592[a,c]	*m*-$NO_2C_6H_4CH_3$	1.93[a,c]
m-$ClC_6H_4CH_3$	0.778	*p*-$C_6H_5OC_6H_4CH_3$	3.421
		m-$C_6H_5OC_6H_4CH_3$	3.463

[a] Taken from "Handbook of Chemistry and Physics", 57th ed., CRC Press, Cleveland, Ohio, 1976. [b] Taken from F. J. Wright, *J. Chem. Eng. Data*, **6**, 454 (1961). [c] Corrected for temperature from a plot of ln η vs. $1/T$.

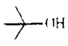
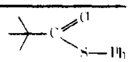
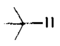
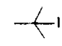
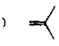
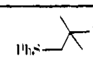
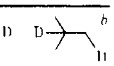
used in the decompositions carried out in the toluenes. Three different samples of thiophenol-*d* were used in the reactions run to determine both the products and the kinetics of the reaction. The results of these experiments are listed in Table II.

Viscosity Measurements. There appeared to be a large amount of product resulting from cage disproportionation (isobutylene and phenyl isobutyl-*2-d* sulfide) whose quantity for a given substrate remained constant at thiol concentrations of 0.1-3 M but whose absolute amount changed for each substrate (see Table I, 0.7-3 M). Since cage effects of this nature can be related to the viscous properties of a solution, the viscosity of the substrates used in the previous study[6,7] and in this study were determined (see Experimental Section, Table III).

Photodecomposition of BPP. The photodecomposition of mixtures of BPP (0.1 M) and thiophenol-*d* (0.7 M) in the desired toluene were carried out and analyzed in the same manner as were the reactions of AIB. The samples were irradiated for varying lengths of time (0.3-6 days). The yield of carbon dioxide for the reactions run for 1-6 days ranged from 41 to 45%, while the yield of *tert*-butyl alcohol ranged from 77 to 95%. An analysis of the remaining gaseous products, produced from these decompositions, showed isobutane, isobutane-*d*, isobutylene, dideuterioisobutane, and the addition product phenyl isobutyl-*2-d* sulfide. These products accounted for 43-78% of the products produced from the peroxide which had decomposed to yield carbon dioxide. The IR spectrum of the mixture after reaction, in solvent *p*-chlorotoluene, showed a new carbonyl absorption at 1710 cm^{-1} (1700 cm^{-1}, toluene) which appeared at lower frequency than the carbonyl absorption due to the starting BPP, 1780 cm^{-1} (1770 cm^{-1}, toluene). The absorption at 1780 cm^{-1} (1770 cm^{-1}) had entirely disappeared. The carbonyl-containing compound (IR 1700 cm^{-1}, toluene) was shown, by a comparison of its IR spectrum and GLC retention time with those of an authentic sample, to be the thiophenyl ester of pivalic acid. The thioester and the CO$_2$ accounted for 86-97% of the initial BPP. The mass spectral analysis of the mixtures of isobutane-*d* (see below) was complicated by the presence of substantial amounts (~4-6%/mol CO$_2$) of a dideuterated isobutane. Elemental sulfur became a visible product at longer irradiation times (>40 h). The results of these analyses as well as those for the reactions carried out to low conversion (17-, 8-, or 6-h irradiation) are listed in Table IV.

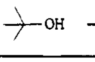
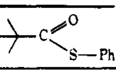
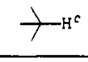
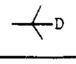
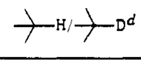
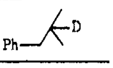
Thermolysis of BPP. The thermal decomposition of BPP in mixtures of thiophenol-*d* and the desired toluene were carried out and analyzed in the same manner as were the photoinitiated reactions. The reaction mixtures, which were protected from light, were thermostated at 55 °C for 96 h. The results

Table IV. Photodecomposition of BPP (30 °C)

substrate ArCH$_3$	starting material, mol/L × 10^2			irradn time, h	CO$_2$	products, mol/mol BPP × 10^2		products, mol/mol CO$_2$ × 10^2				
	[BPP]	[C_6H_5SD][a]	[ArCH$_3$]									 [b]
$C_6H_5CH_3$	10.7	66.2	821.8	72	42.1	91.6	49.3	29.0	36.3	6.3	0.009	3.7
m-$ClC_6H_4CH_3$	10.3	66.8	764.4	144	44.3	95.4	51.4	31.5	11.2	8.4	0.004	1.8
p-$ClC_6H_4CH_3$	10.6	67.9	767.5	42	40.8	76.9	44.7	30.2	37.1	8.2	0.01	3.3
m-$MeC_6H_4CH_3$	10.3	64.8	721.7	72	42.8	93.8	49.9	32.5	13.6	9.4	0.008	
p-$MeC_6H_4CH_3$	10.3	67.2	713.1	72	43.2			33.7	12.7	10.8		
								C_4H_{10}/C_4H_9D				
$C_6H_5CH_3$	10.3	65.2	850.8	17				0.6746				
$C_6H_5CH_3$	10.3	68.9[c]	856.6	8				0.7128				
$C_6H_5CH_3$	10.4	73.5[c]	837.2	6				0.6971				
p-$MeC_6H_4CH_3$	10.5	63.7	737.4	17				0.8140				
p-$MeC_6H_4CH_3$	10.3	67.7[c]	703.2	8				0.8451				
m-$MeC_6H_4CH_3$	10.2	68.3[c]	734.7	8				0.7680				
p-$ClC_6H_4CH_3$	10.2	67.5[c]	763.1	8				0.7284				
p-$ClC_6H_4CH_3$	10.3	77.0[c]	761.4	6				0.7199				
m-$ClC_6H_4CH_3$	10.3	66.8[c]	741.8	8				0.7533				
p-$CNC_6H_4CH_3$	10.5	66.3	761.7	17				0.9649				
p-$CNC_6H_4CH_3$	10.6	77.0[c]	745.5	6				1.4878				

[a] Sample 2 of the thiophenol-*d* (see Table I). [b] $C_4H_8D_2$ represents a minimum value for this concentration while C_4H_{10} and C_4H_9D are maximum values; see Discussion and Experimental Section. [c] Sample 3 of the thiophenol-*d* (see Table II).

Table V. Thermodecomposition of BPP at 55 °C (96 h)[a]

substrate	starting material, mol/L × 10²				products, mol/mol × 10²		products, mol/mol CO_2 × 10²				
$ArCH_3$	[BPP]	$[C_6H_5SD]$[b]	$[ArCH_3]$	CO_2			 [c]		 [d]		
$C_6H_5CH_3$	10.4	66.0	819.8						0.2577 (0.0847)		
$C_6H_5CH_3$	10.4	65.9	845.4	47.4	93.4	44.8	17.0 (5.7)	65.3	0.2610 (0.0880)	12.8	11.9
p-$MeC_6H_4CH_3$	10.4	66.9	733.6						0.2568 (0.0838)		
p-$MeC_6H_4CH_3$	10.4	65.6	712.1	46.4	96.2	52.7	15.9 (6.1)	56.6	0.2795 (0.1065)	11.9	10.4
m-$MeC_6H_4CH_3$	10.3	65.9	729.8						0.2379 (0.0649)		
m-$MeC_6H_4CH_3$	10.2	66.0	739.9	48.3	97.4	47.2	16.0 (5.0)	63.5	0.2527 (0.0797)	10.8	14.5
p-$ClC_6H_4CH_3$	10.4	65.5	766.3						0.3114 (0.1384)		
p-$ClC_6H_4CH_3$	10.4	67.9	737.9	42.6	94.2	53.2	16.7 (5.8)	62.8	0.2651 (0.0921)	10.8	13.1
m-$ClC_6H_4CH_3$	10.1	62.2	740.7	43.8	95.7	51.3	15.5 (4.2)	65.0	0.2384 (0.0654)	12.2	14.9
m-$ClC_6H_4CH_3$	10.5	67.1	761.3	45.9	95.1	49.5	16.8 (5.6)	64.5	0.2600 (0.0870)	10.4	16.1
p-$CNC_6H_4CH_3$	10.4	64.5	743.9						1.0774 (0.9044)		
p-$CNC_6H_4CH_3$	10.6	67.9	749.2	47.2	94.9	46.7	37.2 (29.8)	43.0	0.8645 (0.6915)	12.6	12.4
p-$PhOC_6H_4CH_3$	10.4	69.1	513.6	32.4	94.1	61.4	26.1 (15.7)	60.0	0.4350 (0.2620)	8.3	14.3
p-$PhOC_6H_4CH_3$	10.4	68.3	515.3	35.1	96.7	61.8	22.3 (12.7)	55.3	0.4042 (0.2312)	9.0	13.4
m-$PhOC_6H_4CH_3$	10.3	70.8	510.9	34.6	95.8	61.6	18.5 (7.7)	62.5	0.2883 (0.1153)	5.7	17.8
m-$PhOC_6H_4CH_3$	10.5	67.1	511.6	35.2	96.1	60.8	17.6 (7.0)	61.2	0.2875 (0.1145)	5.8	18.4
Freon 112	10.6	67.4							0.2058		
Freon 112	10.6	68.3							0.2158		

[a] The reactions showed a material balance for *tert*-butyl radicals produced (the portion of the reaction yielding CO_2) of 99 ± 3%; a small correction was made for the isobutylene produced from the dehydration of the missing *tert*-butyl alcohol (3–7%). [b] Sample 3 of the thiophenol-*d* was used (see Table II). [c] Values in parentheses are corrected for abstraction from thiophenol in the thiophenol-*d* (sample 3) by the subtraction of (0.173 × amount of C_4H_9D) from the total C_4H_{10}. The correction value 0.173 is the average fraction of protium obtained from the decomposition run in Freon; see last two entries in Table V. [d] Analysis by *m/e* ions 59 (see Discussion). The ratios listed are for the uncorrected values. The values in parentheses are the correct values.

obtained from the analyses of these reactions are listed in Table V.

Mass Spectral Analysis of Isobutane and Isobutane-*d*. The mass spectral cracking pattern of isobutane and isobutane-*d* shows only weak intensity parent ion peaks, *m/e* 58 and 59 (2.73% of the base peak), while the fragment ions, *m/e* 43 and 44, are the most abundant ions in the spectrum.[18] For this reason Pryor and Davis[6,7] used the ratio of the fragment ions (M − 15) to determine the ratio of products C_4H_{10} to C_4H_9D. Implicit in the use of these fragment ions to determine this ratio are a number of assumptions which may or may not be true. In using the fragment ions for this analysis the assumptions made are (1) that there is no isotope effect influencing the cracking patterns of C_4H_{10} and C_4H_9D, (2) that since it has been reported that the M − 15 fragment produced from the ionization of isobutane results from the loss not only of the methyl carbons but the central carbon as well (by a rearrangement process which also involves hydrogen migration) it is assumed that the rearrangement correction must be constant for repetitive analysis,[19] (3) that the fragment at nominal mass *m/e* 43 (a common fragment produced in many systems by impurities) was due solely to the ionization of isobutane, (4) that there is a constant contribution to the cracking pattern of isobutane or isobutane-*d* of the M − 16 fragment, which in the case of isobutane-*d* yields a fragment ion at *m/e* 43. The latter assumption is not justified, however, since it implies a constant source temperature, sample pressure, and repeller field. Since the validity of any one of the assumptions listed above is in doubt, the analyses of the product ratio $[C_4H_{10}]/[C_4H_9D]$ were carried out by the more unambiguous measurement of the parent M^+ ions. The determinations could be made at very high resolution (1/25 000 atomic mass units) by measuring the ratio of the contributions of the $C_3C^{13}H_{10}$ (*m/e* 59.081 605) and C_4H_9D (*m/e* 59.084 527) ions to the *m/e* 59 peak and calculating the amount of C_4H_{10} present by a correction for the natural abundance of ^{13}C ($^{12}C/^{13}C$ = 98.888/1.112 × 4).

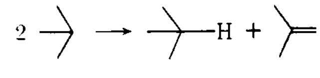
When the analysis of the products was carried out for the C_4H_{10} and C_4H_9D mixtures produced from the photodecomposition of BPP (longer reaction times) the parent ions, nominal mass *m/e* 59, contained a further component (*m/e* 59.082 979) which was assigned as the M − 1 fragment ion of the compound $C_4H_8D_2$. At high resolution the fragment ions M − 15 were both shown to have only single components if CO_2 (*m/e* 44) was resolved and therefore the analysis of the gases from the perester decompositions was carried out using both the resolved fragment ions (*m/e* 43/44) and the resolved parent ions (*m/e* 59). The two methods using the *m/e* 59 and 43/44 fragment ions do not give the same results (see Discussion section).

The analysis of the C_4H_{10} and C_4H_9D obtained from the thermolysis of BPP was less complicated than the analysis of the mixtures obtained from the photolysis reactions since the products were not admixed with $C_4H_8D_2$; therefore the mixture composition could be determined using the mass *m/e* 59 molecular ions.

Discussion

AIB Decompositions. Relative reactivities from the data, examples of which are listed in Table I, for the decomposition reactions of toluene solutions of AIB, 3 and 0.7 M in thiophenol-*d*, were calculated in the usual manner.[10] Hammett plots of log $k_a/k_a{}^0$ vs. the substituent constants, σ, give excellent correlations [(3 M) PhSD, S_ρ = −0.06, r = 0.96; (0.7 M) PhSD, S_ρ = −0.06, r = 0.94] when the values for the *m*- and *p*-phenoxytoluenes are excluded. The ρ values obtained are positive, in agreement with Pryor and Davis,[6,7] although their magnitudes (+0.53 and +0.55) are not so large as that previously reported, +1.0. This discrepancy was attributable, however, to the difference in the method of mass spectral analysis (see Results section), since when the ratio of $[C_4H_{10}]/[C_4H_9D]$ was determined using the fragment ions *m/e* 43/44 the ρ value found for the reactions carried out with 3 M thiophenol-*d* was, as reported,[6] + 0.99.

If one examines the data given in Table I it is immediately obvious that very little, if any, of the isobutane arises from the abstraction reactions of a *tert*-butyl radical from a toluene. A large amount of the *tert*-butyl radicals (~25%) abstract deuterium from thiophenol-*d*. The major portion of the remaining *tert*-butyl radicals appears to disproportionate to form isobutylene plus its disproportionation partner isobutane. The isobutylene plus its addition product and an equivalent amount of isobutane formed by disproportionation account for 71–95% of the *tert*-butyl radicals that do not form deuterated isobutane (see column headed "uncorrected maximum abstraction from



$ArCH_3$"). The disproportionation reaction was shown to be a cage process since, for each individual substrate, the absolute amount of isobutylene formed (isobutylene plus its addition product phenyl isobutyl sulfide) remained constant at concentrations of scavenger, thiophenol-*d*, of 0.1–3 M. It is not surprising that *tert*-butyl radicals readily react with thiophenol rather than toluene, or that in fact they undergo bimolecular reaction rather than competitive abstraction from toluene. Chain transfer data for a variety of structurally different polymer radicals invariably show that they react with thiols $>10^4$ times faster than with toluene;[20] any values of relative reactivity much different than this would be suspect. Further the actual rate constant for the reaction of poly(vinyl acetate) radicals with toluene is only 5 $M^{-1}\ s^{-1}$ at 60 °C (and for the polystyryl radical $1.8 \times 10^{-3}\ M^{-1}\ s^{-1}$).[21] Accordingly only at very low rates of radical production should the abstraction reaction of a *tert*-butyl radical compete with bimolecular radical disappearance ($k = 2 \times 10^9\ M^{-1}\ s^{-1}$).[22]

The disproportionation–combination ratio was found to be 6.0 ± 1.4 for the reactions run with 0.1–3 M thiol. The value is in reasonable agreement with the ratios previously reported by others for solution-phase reactions, 4.5 (solvent benzene, 20–60 °C)[23] and 7.2 (solvent pentane, 30 °C).[24] The absolute amount of combination product was found to be almost ten times larger than that reported by Pryor and Davis.[6,7] This discrepancy may be due to the large error present in the GLC analysis of the combination product, 2,2,3,3-tetramethylbutane. The hydrocarbon is highly volatile, and unless more than usual care was taken low values were obtained.

The maximum amount of isobutane actually formed from benzylic abstraction could be estimated by carrying out the photodecomposition of AIB in an inert solvent, Freon 113, in the presence of 3 M thiophenol-*d* (see Table II). Abstraction from the thiophenol impurity in the thiophenol-*d*, after the correction for the amount of isobutane formed by disproportionation, amounted to 24 (sample 1), 42 (sample 2), and 21% (sample 3) of the isobutane-*d* formed in the reaction. When this fraction of the isobutane was substracted from the uncorrected maximum amount of abstraction only 0–16% of the isobutane formed in any of the reactions which were useful for the kinetic analysis (0.6–3 M C_6H_5SD) was found to be attributable to benzylic abstraction (see Table I, last column). The corrected values of log $k_a/k_a{}^0$ did not give a linear correlation ($r = 0.24$) with σ. It was not surprising that the correction factor (0.21, 0.24, or 0.42) for abstraction of protium from the impurity present in the deuterated thiophenol was so large since a reasonable estimate[25] for the isotope effect for abstraction from thiophenol and thiophenol-*d* of $k_H/k_D \sim 5$ would place the purity of the thiophenol-*d* at approximately 95 (sample 1), 92 (sample 2), and 96% D (sample 3).

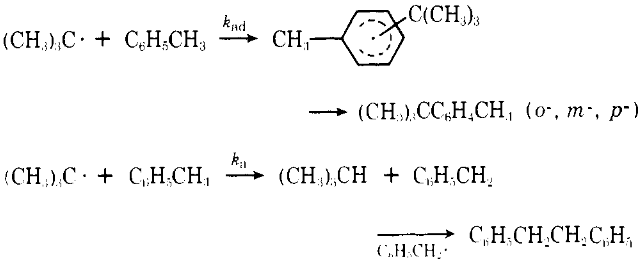
A further indication that in this system benzylic hydrogen abstraction is a negligible reaction comes from the results of the photodecomposition of AIB in neat toluene. The reaction was found to yield *tert*-butyltoluene and bibenzyl. Since both products arise from the reaction of precursor radicals formed from the bimolecular reaction of a *tert*-butyl radical and a toluene molecule, both precursor radicals should be formed in a definite ratio regardless of the number of *tert*-butyl radicals which are scavenged. When thiophenol was added to the reaction mixture no bibenzyl or *tert*-butyltoluene was detected (GLC). The absence of bibenzyl would be expected since it would have to be produced from the coupling of two radicals in the presence of an efficient scavenger, thiophenol. However, if abstraction from toluene had taken place then a detectable amount of *tert*-butyltoluene should have been detected since the addition product and the bibenzyl are formed in a ratio of ~ 1.5 (k_a/k_{ad}). Since a material balance is obtained, no detectable amount of addition product is formed and therefore no appreciable abstraction from toluene had taken place. The validity of this argument, however, does depend on the reasonable assumption that the addition reaction is irreversible under the reaction conditions.

As disproportionation has been shown to be the major source of isobutane it is necessary to reexamine the kinetic assumptions made in the previous investigation.[6,7] The authors derive the expression of the relative rates of appearance of isobutane and deuterated isobutane:[7]

$$\frac{d[C_3H_{10}]/dt}{d[C_3H_9D]dt} = \frac{k_a[ArCH_3]}{k_{SD}[RSD]} + \frac{k_{SH}[RSH]}{k_{SD}[RSD]} + \frac{k_d f_c[\text{initiator}]}{k_{SD}[C_4H_9\cdot][RSD]} + \frac{k_d'[C_4H_9\cdot]}{k_{SD}[RSD]}$$

The assumption that the last two terms in the equation (the disproportionation terms) are negligible allowed them to integrate the expression and to use the integrated fcrm to obtain kinetic values for k_a/k_{SD}. Since the third term in the equation (cage disproportionation) has now been shown to be the major term, the expression does not appear to be easily integratable.

Since all, or nearly all, of the isobutane formed in the reactions was attributable to a disproportionation reaction (after a correction for abstraction from thiophenol, which is relatively constant in reactions run with the same sample of thiophenol-*d* at approximately the same concentrations), and since the ratio of rate constants, k_a/k_{SD}, obtained by determining the ratio of products $[C_4H_{10}]/[C_4H_9D]$ varied in a systematic manner from substrate to substrate, it must be concluded that some property of the substrate, which is in effect the solvent for the reaction, must be controlling the amount of disproportionation which takes place. The property of the substrate (solvent) most likely to effect this change was its viscosity. A list of viscosities (30 °C) of the substituted toluenes is given in Table III. A plot of the logarithm of the viscosity of each substrate relative to toluene vs. the substituent constant, σ, for each substituent is given in Figure 1. The plot, if one excludes the *m*- and *p*-phenoxytoluene, gives a surprisingly good correlation, $r = 0.92$, $S_y = 0.08$, and its slope, $\rho = 0.61$, is the same within experimental error as that obtained from the plots of the logarithm of the relative rates $k_a/k_a{}^0$ vs. σ.



In order to further substantiate the effect of the viscosity of the substrates (solvents) on the quantity of cage disproportionation and to explain why the two substrates (*m*- and *p*-phenoxytoluene) with high viscosities did not fit the Hammett treatment for plots of log ($k_a/k_a{}^0$) vs. σ or the plot of log η/η^0 vs. σ (see Figure 1) a plot was constructed of the fluidity of the solvent, $1/\eta$, vs. the cage efficiency, 1/olefin concentration (see Figure 2). The plot gave an excellent correlation, $r = 0.97$, and clearly demonstrated that the cage yield of isobutane, the major fraction of isobutane formed, was directly controlled by the viscosity of the solvent.

The viscosity of the solvents are obviously changed by the addition of thiophenol-*d*. At low concentrations, 0.1–0.8 M, of thiol the relative viscosities are only negligibly changed. At the high concentration of thiol, 3 M, the viscosities of the solvents change appreciably (from 4 to 25%); however, a plot of the relative viscosities of the mixtures gave an excellent cor-

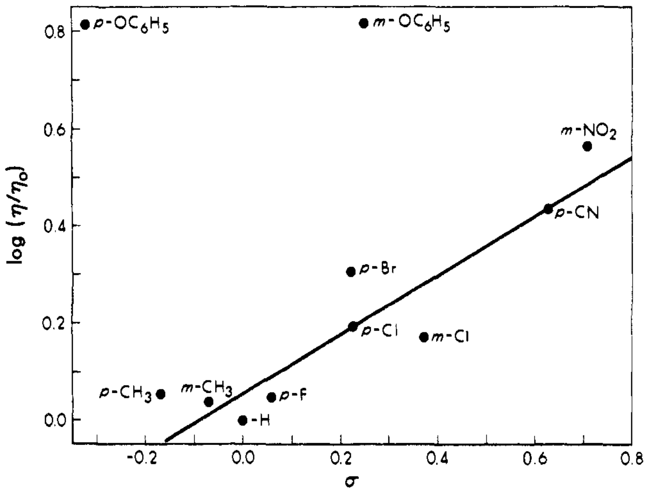


Figure 1. A Hammett equation plot of the log (relative viscosities of the substituted toluenes to that of toluene) vs. σ, 30 °C. A linear regression analysis gave $\rho = 0.60$, $r = 0.92$, $S_{yx} = 0.082$, when the values of *p*- and *m*-phenoxytoluene were not included.

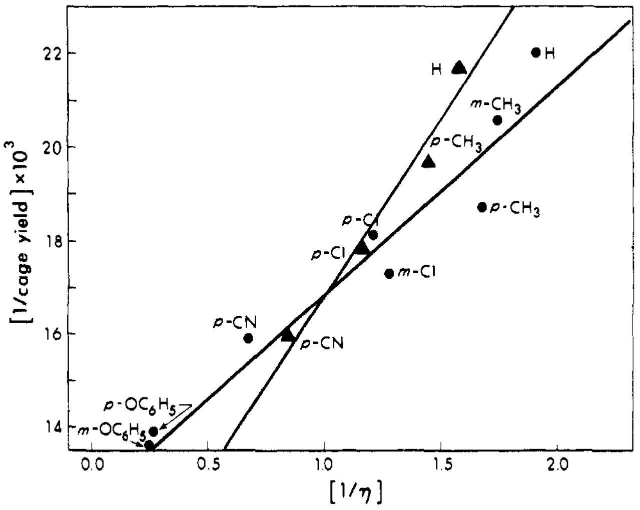


Figure 2. A plot of fluidity of the solvent ($1/\eta$) vs. cage efficiency (1/cage yield). The values indicated by ● are the average cage yield at low thiol concentrations, 0.1–0.8 M, $r = 0.97$. The values indicated by ▲ are average values for reactions carried out at 3 M thiol, $r = 0.96$.

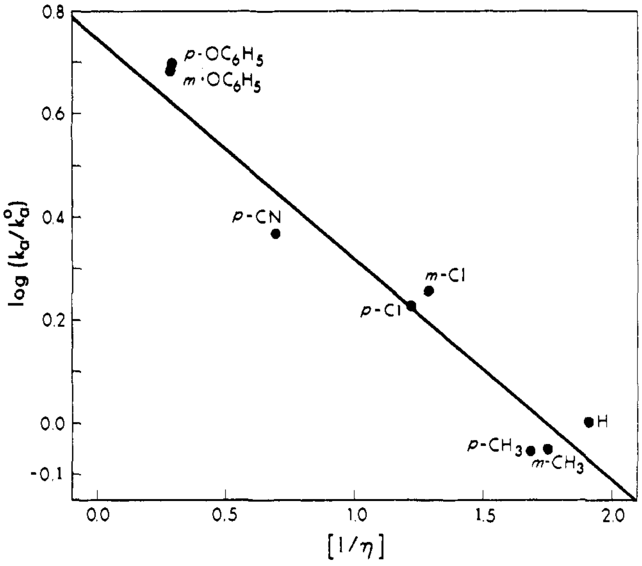


Figure 3. A plot of log (k_a/k_a^0), corrected for abstraction from thiophenol, vs. $1/\eta$ for the photodecomposition reactions of AIB with added thiophenol-*d* (0.7 M). A linear regression analysis gave a linear correlation, $r = 0.98$.

relation with σ substituent constants ($r = 0.92$). Further a plot of the fluidities of the 3 M mixtures vs. the cage efficiencies of duplicate runs carried out using 3 M concentrations of thiophenol-*d* gave an excellent correlation ($r = 0.96$) showing, as anticipated, a somewhat larger slope than the correlation for the reactions carried out using lower concentrations of thiol (see Figure 2).

Since *m*- and *p*-phenoxytoluene are both solvents of relatively high viscosity it was not surprising[26] that they did not fit the correlations given in Figure 1. A plot of the relative reactivity data, uncorrected for disproportionation, but corrected for abstraction from thiophenol, vs. the fluidity of all of the substrates (solvents) gave an excellent linear correlation ($r = 0.98$); see Figure 3.

BPP Decompositions. The observation that at thiol concentrations of 0.1–3 M *tert*-butyl radicals generated in the AIB decompositions will not competitively abstract a benzylic hydrogen from toluene makes it necessary to conclude that *tert*-butyl radicals generated from an alternative source, BPP, will behave similarly. Since it is believed that the cage decomposition products of BPP do not yield isobutane,[28] the observation by Pryor and Davis[6] that the relative rates derived from the perester decomposition also correlate with σ is an anomaly and, therefore, must be due to effects other than the solvent viscosity.

From our previous studies on the thermal decomposition of BPP[13,14] it was known that, when thiophenol was used as a radical scavenger, a reaction occurred between the perester and the thiol, presumably ionic, to yield the thiophenyl ester of pivalic acid. It was not surprising that under the conditions of the photochemical decomposition reactions (2–6 days, 30 °C) the ester was formed in appreciable amounts. The perester that does decompose (40–45%) yielded isobutane, isobutane-*d*, and dideuterated isobutane as well as the cage product isobutylene; see Table IV. The addition product phenyl isobutyl-*2-d* sulfide was only found in small amounts; however, a material balance could not be obtained on the system (see Table IV). A reasonable proposal for the genesis of the dideuterated isobutane could be consistent with this observation, since at the longer irradiation times necessary for the decomposition of the perester the photolysis of phenyl isobutyl-*2-d* sulfide can give a deuterated radical which upon transfer with thiophenol-*d* could yield the dideuterated isobutane. This suggestion was shown to be correct since the photolysis of phenyl isobutyl sulfide, under the reaction conditions used for the photolysis of BPP (30 °C, 168 h, 0.6 M thiophenol-*d*), yielded isobutane and isobutane-*d* as the major products.

A plot of log (k_a/k_a^0), obtained from the data for the BPP decompositions using the mass spectral analysis of the C_4H_{10} to C_4H_9D ratios vs. σ, did not give a satisfactory correlation. Since the previous authors[6,7] only obtained four points for this system the correlation of these points to those obtained in the AIB system may have been fortuitous.

The thermal decomposition of BPP was investigated since an analysis of the results of its photolysis had a number of limitations; e.g., the production of $C_4H_8D_2$ which interfered with the mass spectral analysis, the observation that the relative rates obtained were dependent upon the irradiation time, and that no material balance could be obtained. The mixtures of BPP, solvent toluene, and thiophenol-*d* were thermostated at 55 °C in the absence of light and allowed to react for 9 half-lives (96 h) for the decomposition of the BPP.[13] The products from the reaction were the same as were found from the photolysis reactions with the exception of the absence of $C_4H_8D_2$ (see Table V). The material balance for the portion of the reaction which yielded the *tert*-butyl radicals, the portion of the reaction yielding CO_2, accounted for 99 ± 3% of the *tert*-butyl radicals that were produced. A plot of the corrected values (corrected for abstraction from thiophenol) for log $(k_a/k_a{}^0)$ vs. σ did not give a satisfactory Hammett correlation, $r = 0.41$ (see data Table V).

Conclusions

The importance of polar effects in free-radical hydrogen abstraction reactions from substituted alkanes has been repeatedly demonstrated.[29] The suggestion that these effects may be interpreted as being governed solely by the effect of the substituents on the bond strength of the bonds made and broken, ΔH, cannot accommodate the experimental data,[29] i.e., the reversal of isomer distribution patterns found for the reactions of different polar radicals on a particular substrate.

The demonstrated nonlinearity of the correlation between ΔH and ρ (all negative ρ values) obtained for benzylic hydrogen abstraction renders the BDE suggestion untenable for these reactions.[30] The demonstration that nucleophilic radicals will give a positive ρ would further substantiate the importance of polar effects in governing the reactivity of these radicals; however, it seems doubtful that any authentic positive ρ values have, as yet, been reported for benzylic hydrogen abstraction.

The positive ρ value reported for the undecyl[8,9] radical has been seriously questioned by Zavitsas.[31]

The positive ρ value reported for *tert*-butyl radicals[6,7] has been shown (this work) to either show no correlation (BPP decompositions) or to be an artifact of an experimentally observed cage disproportionation reaction (AIB decompositions). The relatively selective *tert*-butyl radical does not abstract hydrogen from solvent toluene (8–6 M) in competition with its abstraction of deuterium from thiophenol-*d* at concentrations ranging from 0.6 to 3 M. At lower concentrations of thiophenol-*d* (~0.1 M) the reaction begins to be measurably competitive; however, the concentration of thiophenol-*d* cannot be approximated as constant and the kinetic expression could not be evaluated in the manner used. From the data listed in Tables I and V it appears that the amount of benzylic abstraction (after correction) was appreciably higher for the substrate, *p*-cyanotoluene; however, this is only a qualitative observation since the values are only a factor of 2 different from the same values listed for *p*-phenoxytoluene. The previously reported[7] observation of a positive ρ value for isopropyl radical abstraction was obtained in the same manner as was that for the *tert*-butyl radical, the photodecomposition of the corresponding azo compound in mixtures of toluenes and thiophenol-*d*. Preliminary results from this laboratory suggest that the positive ρ obtained for these reactions is also, in part, an artifact of a cage disproportionation reaction. This less selective radical, however, may be able to competitively abstract from thiophenol-*d* and a toluene substrate. The only possible exception to the belief that alkyl radicals will show a positive ρ value is the data obtained for the 1-ethylpentyl radical;[10] however, since no product studies or experimental details were reported in this communication, a final judgment on this work must be reserved.

The inability to observe a positive ρ for carbon-centered radicals is most likely due to the small difference in electronegativity (a function of the ionization potential and the electron affinity) between the abstracting radical and its substrate benzylic carbon, while the absence of any correlation (zero ρ or very small negative value) attests to the small effect of small changes in BDEs.

Experimental Section

Materials. Toluene and *p*-xylene (Philips 66 research grade, >99.9%) were fractionally distilled through a packed column and shown by GLC (10 ft × 1/4 in. 10% QF-1 on 60/80 Chromosorb P AW DMSC, glass column) to be >99.9% pure. *m*-Xylene and *m*-chlorotoluene (Eastman Chemical Co.) were fractionally distilled through a 24-in. Teflon spinning band column and shown to be >99.9% pure by GLC (QF-1 column). *p*-Cyanotoluene (bp 92.5 °C, 14 mm) and *p*-chlorotoluene (bp 161.7–161.8 °C, 699 mm) (Aldrich Chemical Co.) were purified by repeated low-temperature fractional recrystallization, fractionally distilled at the temperatures indicated, and checked for purity, >99.9%, by GLC (QF-1 column). *m*-Phenoxytoluene (Aldrich Chemical Co.) was fractionally distilled (bp 107 °C, 3 mm) and shown to be >99.9% pure by GLC (QF-1 column). *p*-Phenoxytoluene was prepared according to the Ullmann ether synthesis[32] and purified by fractional distillation (bp 103–105 °C, 2.5 mm). Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.70; H, 6.62. NMR (CCl_4): δ 2.65 (s, 3 H, $-CH_3$), 8.0–8.65 (m, 9 H, aromatic).

Thiophenol-*d* was prepared by shaking thiophenol (Columbia Organics) with D_2O (Merck Sharp and Dohme, Canada, >99.8% D) four separate times. The thiophenol-*d* samples 1, 2, and 3 were dried over anhydrous $MgSO_4$, decanted, and fractionally distilled under nitrogen (bp 52 °C, 12 mm). Sample 3 of the thiophenol-*d* was stored moist after admixing with 1 mL of D_2O, according to the method of Pryor.[7] The reactions run with sample 3 using the moist thiophenol-*d* showed the material to contain >98% D.

AIB was prepared by the method of Stowell.[33] The azo compound was fractionally distilled through a 24-in. Teflon spinning band column: bp 108 °C (699 mm) (lit. bp 98–109,[33] 109–110 °C[34]); NMR (pentane) δ 1.15 (s, $C(CH_3)_3$).

BPP was prepared according to the method previously reported.[13] Anal. Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 62.05; H, 10.51. $n^{25}{}_D$ 1.4101 (lit.[13] $n^{25}{}_D$ 1.4100).

Isobutyl phenyl sulfide was prepared according to the method of Ipatieff:[35] 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).

Phenyl *tert*-butyl sulfide was prepared by the method reported for the synthesis of *tert*-butyl pentachlorophenyl sulfide:[36] NMR (CCl_4) δ 1.23 (s, 9 H, $-C(CH_3)_3$), 7.18–7.50 (m, 5 H, aromatic); mass spectra $C_{10}H_{14}S$ *m/e* 166. It was shown by its GLC retention time that, when added to reaction mixtures from the AIB or BPP decompositions, it was not a detectable product formed from either reaction.

The thiophenoxy ester of pivalic acid was prepared by the mixture of pivaloyl chloride (0.1 mol) and thiophenol (0.1 mol). The mixture was stirred for 1 h, washed with dilute NaOH several times and then with water, dissolved in CH_2Cl_2, and dried over anhydrous $MgSO_4$ and the solvent was evaporated. IR showed an absorption at 1700 cm^{-1} (toluene).

2,2,3,3-Tetramethylbutane (NBS standard) was used as obtained.

AIB Photodecompositions. A 20-mL quartz tube equipped with a break-seal was washed with chromic acid, water, concentrated NH_4OH, and water and dried. The tube containing several milliliters of D_2O was heated to reflux for several minutes and dried again overnight. Solutions of AIB and thiophenol-*d* were weighed into a volumetric flask and the materials were dissolved in the appropriate toluene to give the desired concentrations. An aliquot of the solution was transferred to the quartz reaction vessel, degassed by the freeze–thaw method, 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) and irradiated for 20 h (30 °C). The reaction vessel was connected to a vacuum line, frozen (−198 °C), opened, and degassed. The noncondensable gas, N_2, was measured with 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 into a trap at −198 °C, the condensable gases C_4H_{10} (C_4H_9D) and C_4H_8 were collected and their total absolute amount was measured in the Toepler pump, and then their relative amounts were determined by vacuum line GLC using a Cow Mac TR-TH thermal conductivity GLC fitted with a 10 ft × 1/4 in. 10% silicon oil 200 on 60/80 Chromosorb W AW glass column at 0 °C. The condensable gases were sealed in break-seals and submitted for mass spectral analysis. The residual reaction mixture was transferred back into the reaction vessel and removed from the vacuum line. A weighed amount of standard (biphenyl) was added to the mixture and the mixture was subjected to GLC analysis (QF-1 column).

The remaining products, 2,2,3,3-tetramethylbutane and phenyl isobutyl-*2-d* sulfide, were identified by their mass spectral cracking pattern and their GLC retention times compared with those of authentic samples (the retention time of the nondeuterated sulfide was used for that of the deuterated material). The mass spectrum of the synthesized sulfide showed a parent peak at *m/e* 166 ($C_{10}H_{14}S$) and no detectable fragmentation at *m/e* 165. The sulfide obtained from the reaction mixture showed a parent ion at *m/e* 167 ($C_{10}H_{13}DS$) and an ion at *m/e* 166 ($C_{10}H_{14}S$). The *m/e* 166/167 ratio was about 10%. The results of a representative number of these analyses are listed in Table I.

BPP Photodecompositions. The reactions of BPP were carried out in the manner described for the AIB decompositions, except that the irradiation times were from two to seven times longer (see Table IV). The reaction mixtures were opened to a vacuum line and the condensable gases were distilled through two traps at −78 °C and condensed in a third trap at −198 °C. The total amount of condensable gases was measured with a Toepler pump and their relative amounts (CO_2, C_4H_{10} (C_4H_9D, $C_4H_8D_2$), C_4H_8) were determined by vacuum line GLC (silicon oil 200 column). The condensable gases were collected and submitted to mass spectral analysis in order to obtain the relative amounts of $C_4H_{10}:C_4H_9D:C_4H_8D_2$.

The remaining material was subjected to GLC analysis, with an added standard, biphenyl (QF-1 column), to determine the amounts of thioester, *tert*-butyl alcohol, and phenyl isobutyl-*2-d* sulfide formed in the reaction mixture. The materials were identified by a comparison of their GLC retention times and their mass spectral cracking patterns with those of authentic samples. The IR spectrum of the reaction mixture showed the carbonyl absorption ($1700\ cm^{-1}$, toluene) of the thioester, while the absorption band for the starting ester was no longer detectable. The results of these analyses are listed in Table IV.

Photolysis of Phenyl Isobutyl Sulfide. A mixture of phenyl isobutyl sulfide (0.0644 M, 0.1283 mmol) and thiophenol-*d* (0.645 M, sample 2) in toluene was irradiated under the same conditions as were used for the photodecomposition of BPP (168 h, 30 °C). Analysis of the reaction mixture showed the production of isobutane (0.0474 mmol, 36.8%), isobutane-*d* (0.0291 mmol, 22.6%), and isobutylene (9×10^{-4} mmol, 0.7%) as well as the unreacted phenyl isobutyl sulfide (0.0428 mmol).

Thermolysis of BPP. The thermal decompositions were carried out and the products analyzed in a manner identical with that of the photolysis reactions, with the exception that the reactions were protected from light and were thermostated at 55 °C for 96 h. The results of these analyses are listed in Table V.

Viscosity Measurements. The viscosities of the substituted toluenes were determined at 30 °C using an Ostwald viscometer, calibrated using distilled water as a standard.[37]

Mass Spectrometry. The high-resolution mass spectrometry was carried out using an AEI-MS50 mass spectrometer apparatus at a resolving power of 25 000. The low-resolution spectra were run using the same instrument, but at a lower resolving power. The GC-mass spectrometry was carried out using an AEI-MS12 coupled to a Varian Aerograph 1400 GC fitted with a 10 ft × ⅛ in. 5% SE-30 on Chromosorb W 80/100 AW column and using an AEI DS50S data system.

GLC Analysis. All quantitative values were determined using standard calibration curves determined using known mixtures of the authentic materials. The relative GC areas for the gaseous samples were determined using the method of peak height × peak width at one-half peak heights, while the areas obtained from the analyses of the liquid fractions were determined using a HP-3380 A integrator.

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