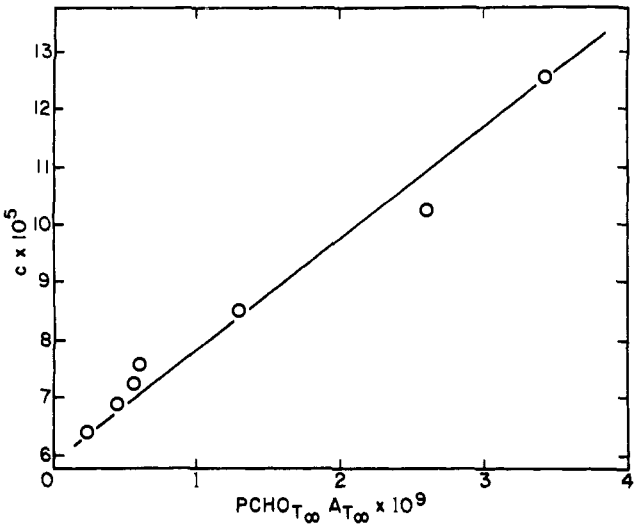

Fig. 2.—The relationship between the c constant (equation 15) and the quantity $PCHOT_{\infty}AT_{\infty}$. Linearity of the plot indicates that the constancy of $k_{obsd}/S''T_{\infty}$ is compatible with the reaction scheme described by equations 7.

morpholine concentration (see Table II). The kinetic scheme as represented by equations 7 is thus seen to predict at least qualitatively the behavior of the transamination reaction in the presence of morpholine. The fact that the value of k_4K_1 obtained in the absence of morpholine (see part I[9]) is almost 40% lower than that obtained in the presence of morpholine reflects the consideration in both treatments of only the kinetically significant rate and equilibrium steps (*i.e.*, the neglect of certain hydration equilibria, etc.). The results show, however, that the transamination reaction is at least as effective when preceded by a 'transimination' reaction in which an imine is converted into an amino acid imine which then undergoes prototropic rearrangement, as is the reaction which involves direct conversion of pyridoxal into the amino acid imine undergoing the prototropic rearrangement. This observation, therefore, suggests that the enzymatic transamination reaction would proceed at least as readily with the pyridoxal phosphate moiety attached to the enzyme surface *via* the aldehyde group and an amino group on the enzyme as with the pyridoxal co-enzyme attached to the protein residue only through the phosphate.

In summary, the "model" for the pyridoxal-requiring transamination reaction, as described in parts I,[9] II[1] and III of this series possesses the following features of enzymological interest: (1) operates in aqueous media; (2) effective at physiological pH values; (3) the reaction is facile at ambient temperatures; (4) employs the weakly basic imidazole and the weakly acidic imidazolium ion as catalysts; (5) does not require metal ions; (6) kinetically similar to enzyme systems in the formation of a complex followed by a rate-determining step affording Michaelis–Menten kinetics; (7) the ability of imidazole to form a catalyst–substrate complex results in a virtual specificity for imidazole at low reactant concentrations compared with other general bases investigated; (8) the transamination reaction in the model system is equally effective if preceded by a transimination reaction; and (9) if it is assumed (a) that the dissociation constants of all the complexes with imidazole and imidazolium ion are quite similar, (b) that the formation constant for aldimine is in the usual range of 1 to 100 and (c) that the acid dissociation constants of intermediates are similar, then it can be calculated[11] that the rate of the prototropic shift leading to the conversion of S_c' to S_c'' is only about 10 to 10^3 times slower than the corresponding step for glutamic-aspartic transaminase.[12]

Experimental

The kinetic procedures have been described in part I.[9] Morpholine (Eastman Kodak, practical) was purified by distillation, after refluxing for 24 hr. over sodium metal, under an atmosphere of dry nitrogen, b.p. 125–126° at 740 mm. (lit.,[13] b.p. 128.3°).

Acknowledgment.—This work was supported by a grant from the National Science Foundation.

(11) T. C. Bruice and R. M. Topping, Proceedings of The Symposium on Pyridoxal Catalysis (Rome, 1962), Pergamon Press, in press.
(12) G. G. Hammes and P. M. Fasella, *J. Am. Chem. Soc.*, in press.
(13) A. L. Wilson, *Ind. Eng. Chem.*, **27**, 867 (1935).

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Reactions of Radicals. V. Reaction of Phenyl Radicals with Aliphatic Disulfides[1-3]

BY WILLIAM A. PRYOR AND PAUL K. PLATT

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Phenyl radicals are generated from phenylazotriphenylmethane at 60° in a series of aliphatic disulfides as solvents. The phenyl radicals react with the disulfides both by attack on hydrogen to give benzene and by attack on sulfur to give a phenyl alkyl sulfide. The ratio of phenyl alkyl sulfide to benzene is determined using gas phase chromatography and is equal to the rate of attack by the phenyl radicals on sulfur *vs.* hydrogen for any given disulfide. The data show that phenyl radicals attack disulfides mainly on sulfur, but that the proportion of the attack on sulfur decreases as the sulfur atom becomes more hindered. Thus, 98% of the attack is on sulfur in methyl disulfide and 49% in *t*-butyl disulfide. Thiols are formed in these reactions, but data can be obtained in regions in which the thiol concentration is too low to affect the product composition. At higher thiol concentrations, an appreciable amount of the benzene is formed from the reaction of phenyl radicals with thiol, and here the relative rate of reaction of phenyl radicals with thiol and disulfide can be obtained. The data show that the phenyl radical reacts 23-fold faster with 2-propanethiol than with isopropyl disulfide, and 8-fold faster with propanethiol than with propyl disulfide. The reactivity of the phenyl radical is discussed.

Introduction

Elucidation of the factors which influence radical reactivity requires a body of data on the rate profile of various radicals with typical organic compounds, and increasing attention is being given to collecting such data. The earliest reactivity profiles were obtained from polymerization transfer studies, in which the growing polymeric radical is allowed to compete between adding another unit of its own monomer and attacking an added transfer agent. Studies of this type have led to data on the reactivity of the polystyryl radical with

(1) Part IV, W. A. Pryor, *Proc. Indiana Acad. Sci.*, in press.
(2) Taken in part from the thesis submitted by P. K. P. in partial fulfillment of the requirements for the degree of Master of Science.
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various substrates[4] including hydrogen donors, disulfides,[5] and peroxides.[6] Somewhat less data are available for the polymeric radicals derived from vinyl acetate[7] and the methacrylate[8] polymers.

The first comparable study of a monomeric radical is that of Edwards and Mayo,[9] who reported the rates of reaction of methyl radicals with a series of hydrogen donors relative to abstraction of a chloride atom from carbon tetrachloride. These data have proved particularly valuable, for example, in comparing radical reactivity in the gas phase and in solution.[10] More recently, several other radicals have received study: The chlorine atom by Russell and Brown[11]; bromine atoms and the succinimidyl radical by Kooyman, Van Helden and Bickel[12]; hydrogen atoms by Hardwick[13]; peroxy radicals by Russell[14]; polysulfenyl radicals by Pryor[15]; trichloromethyl radicals by Kooyman[16] and by Huyser[17]; and the *t*-butoxyl radical by Walling,[18] Williams, *et al.*,[19] Johnston and Williams,[20] and others.[21]

We have initiated a study of the reactivity of the phenyl radical, chosen because it can be generated in high efficiency from phenylazotriphenylmethane (PAT), an azo compound which decomposes at a convenient rate at mild temperatures and has a rate of decomposition which is insensitive to solvent effects. Azo compounds are preferable sources of radicals to peroxides, since the latter are subject to induced decomposition. In the Edwards and Mayo study, acetyl peroxide was used as the source of methyl radicals and considerable amounts of induced decomposition made accurate determination of relative rates more difficult. In addition, the phenyl radical is an important radical which gives unambiguous, easily identified products, but which has not been studied.

The first series of substances examined were the aliphatic disulfides, and these data are reported here. In these compounds attack can occur on either hydrogen or on sulfur. The technique involves dissolving PAT in

$$C_6H_5\cdot + RR'HCSSCHRR' \begin{cases} \xrightarrow{k_{1a}} C_6H_5{-}SCHRR' + RR'CHS\cdot & (1a) \\ \xrightarrow{k_{1b}} C_6H_5H + RR'CHSS\dot{C}RR' & (1b) \end{cases}$$

the disulfide, allowing it to completely decompose at 60°, and analyzing the reaction products by gas phase chromatography (g.p.c.) for the phenyl alkyl sulfide/benzene ratio. This ratio gives the relative rate of reaction 1a to 1b.

Experimental

Phenylazotriphenylmethane (PAT).—The azo compound was prepared by the method of Solomon, Wang and Cohen.[22] The yield of the intermediate hydrazo compound was typically 68%, and this was allowed to air oxidize by dissolving in a large excess of ether and removing the ether under vacuum below 25°. The crude PAT was dissolved in a minimal amount of benzene, diluted with an equal volume of absolute ethanol, allowed to stand at 0°, and the crystals of PAT filtered. Recrystallization was repeated until the melting point was constant. In order to ensure the complete removal of benzene (which is one of the reaction products), approximately 2 g. of PAT was dissolved in 1 liter of absolute ethanol, the solution concentrated to 250 ml. under vacuum at 0°, and the PAT filtered and dried under vacuum. The final melting point is 111–112° with decomposition, in agreement with literature values.[22,23] The ultraviolet spectrum is in agreement with that of Alder and Leffler.[23c] Decomposition of PAT in carbon tetrachloride solvent gave no benzene as product showing the absence of benzene in the PAT.[24]

Sulfur Compounds.—The disulfides are all commercially available and were purified by repeated distillation at a 50:1 reflux ratio until the g.p.c. spectra were satisfactory. The properties of the disulfides are summarized in Table I. Their b.p., n.m.r. spectra, elemental analysis and refractive index agreed with the literature or with expected values. The purity of the disulfides to g.p.c. is critical in the analytical scheme used here since small amounts of benzene and phenyl alkyl sulfide must be detected in the disulfides as solvents. The purities given are based on g.p.c. areas, a valid procedure since detector response is relatively insensitive to the nature of the substrate in analysis by thermal conductivity using helium as carrier gas. The phenyl alkyl sulfide knowns were prepared by a method based on that of Ipatieff, Pines and Friedman[25]; yields and physical properties are given in Table I.

TABLE I

PROPERTIES OF COMPOUNDS USED

Compound	Source[a]	Yield, %	B.p., °C. (mm.)	$n^{25}D$	Purity,[c] %
Propanethiol	E.K.	..	...	0.8360	..
2-Propanethiol	E.K.	..	...	0.809	..
Methyl phenyl sulfide	Col.	..	...	1.5834	98.7
Propyl phenyl sulfide	[a]	65	106 (19)	1.5545[b]	99.9
Isopropyl phenyl sulfide	[a]	71	95 (17)	1.5444	99.9
Butyl phenyl sulfide	[a]	79	93.0–94.0 (3)	1.5441	99.8
sec-Butyl phenyl sulfide	[a]	57	104 (14)	1.5420[b]	99.9
Isobutyl phenyl sulfide	[a]	68	109–112 (15)	1.5413	99.4
t-Butyl phenyl sulfide	[a]	48	91.8–92.0 (14)	1.5305	98.7
Methyl disulfide	E.K.	..	108	1.5232	99.9
Propyl disulfide	Col.	..	69.5–72.2 (10)	1.4982[b]	99.8
Isopropyl disulfide	Col.	..	76.0 (28)	1.4890	99.7
Butyl disulfide	E.K.	..	94.8 (6)	1.4904	99.9
sec-Butyl disulfide	Col.	..	73.2–76.8 (4)	1.4902	99.8
Isobutyl disulfide	E.K.	..	92.5–94.0 (13)	1.4842	99.9
t-Butyl disulfide	E.K.	..	77.0–79.0 (14)	1.4875	99.9

[a] E.K. = Eastman Kodak Chemicals Division; Col. = Columbia Organic Chemicals Co. The phenyl alkyl sulfides were prepared by a method based on that of Ipatieff, Pines and Friedman. Yields are given in the next column. [b] At 20°. [c] Purity is by g.p.c. peak area; see Experimental.

Gas Chromatographic Analysis (g.p.c.).—A Wilkens Aerograph Hy-Fi g.p.c. with flame ionization detector was used. The recorder was a Sargent model SR equipped with disk integrator, but integration using a planimeter was found more accurate. A 6-foot column packed with 30% Carbowax 20M on 60/80 mesh firebrick was used. Constant amounts of solution were injected using a Hamilton 10 mμ syringe with a Chaney adaptor. A calibration graph was prepared for each compound giving peak area *vs.* molarity, and the concentrations of products could then be determined directly as molarities. Analysis of unknown reaction mixtures was always immediately preceded and followed

(4) See the reviews by: (a) G. Henrici-Olivé and S. Olivé, *Fortschr. Hochpolym.-Forsch.*, **2**, 496 (1961); (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 148–160; (c) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 46–57, 75–93.

(5) W. A. Pryor and T. L. Pickering, *J. Am. Chem. Soc.*, **84**, 2705 (1962).

(6) (a) W. A. Pryor and E. P. Pultinas, *ibid.*, **85**, 133 (1963); (b) W. A. Pryor, *J. Phys. Chem.*, **67**, 519 (1963).

(7) See ref. 4a; also J. T. Clarke, R. O. Howard and W. H. Stockmayer, *Makromol. Chem.*, **44–46**, 427 (1961).

(8) See ref. 4a; also see S. N. Khanna, S. R. Chatterjee, U. S. Nandi and S. R. Palit, *Trans. Faraday Soc.*, **58**, 1827 (1962).

(9) F. G. Edwards and F. R. Mayo, *J. Am. Chem. Soc.*, **72**, 1265 (1950).

(10) *E.g.*, see, A. F. Trotman-Dickenson, "Free Radicals," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 70.

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(14) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

(15) W. A. Pryor, *ibid.*, **82**, 2715 (1960); also see ref. 4c, p. 144.

(16) E. C. Kooyman, *Discussions Faraday Soc.*, **10**, 163 (1951).

(17) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960).

(18) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108 (1960); **82**, 6113 (1960); C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

(19) A. L. Williams, E. A. Oberright and J. W. Brooks, *ibid.*, **78**, 1190 (1956).

(20) K. M. Johnston and G. H. Williams, *Chem. Ind.* (London), 328 (1958); *J. Chem. Soc.*, 1446 (1960).

(21) J. H. T. Brook, *Trans. Faraday Soc.*, **53**, 327 (1957); G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959).

(22) S. Solomon, C. H. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, **79**, 4104 (1957).

(23) (a) G. L. Davies, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 4397 (1956); (b) R. N. Chadha and G. S. Misra, *Makromol. Chem.*, **14**, 97 (1954); (c) M. G. Alder and J. E. Leffler, *J. Am. Chem. Soc.*, **76**, 1425 (1954).

(24) Spectrum and runs in carbon tetrachloride solvent are unpublished data by H. Guard of this Laboratory.

(25) V. N. Ipatieff, H. Pines and B. S. Friedman, *J. Am. Chem. Soc.*, **60**, 2731 (1938). Alkyl bromides were used in place of the olefins except for phenyl *t*-butyl sulfide, where *t*-butyl alcohol was used.

by the known standards. Reproducibility was better than 0.5%. All solutions were prepared at 30.0° in ampoules made from 8-mm. tubing, the solutions were frozen in liquid nitrogen and deaired in the standard manner,[5] and runs were analyzed immediately upon being opened.

Results

From eq. 1a and 1b

$$R = \frac{k_{1a}}{k_{1b}} = \frac{d(RSC_6H_5)}{d(C_6H_5H)} \cong \frac{RSC_6H_5 \text{ formed}}{\text{Benzene formed}}$$

where R is the ratio of attack by phenyl radicals on sulfur to hydrogen for a particular disulfide, k_{1a} is the rate constant for eq. 1a, k_{1b} for eq. 1b, and $k_1 = k_{1a} + k_{1b}$. Therefore, $R/(1 + R)$ is the fraction of the attack which occurs on sulfur. Initially it was hoped to analyze runs at less than 100% decomposition of PAT; however, it was found that any remaining PAT decomposed in the g.p.c. All analyses therefore were done at 100% reaction, and the effect of varying the PAT concentration was examined by changing its initial concentration.[26]

The most detailed data were obtained for propyl and isopropyl disulfides, and these data are given in Tables II and III. The data show that R for propyl disulfide is 9.3 over a 20-fold variation in the initial concentration of PAT, and that R for isopropyl disulfide is 1.79 over a 100-fold range in PAT concentration. The value of R shows no dependence on the initial concentration of PAT. This implies that the phenyl radicals are reacting almost exclusively with solvent and that an insignificant fraction reacts with secondary products. If appreciable reaction occurred with secondary products, R would depend on PAT concentration since the concentration of secondary products varies with PAT concentration. Analysis also shows that thiol is a product.

TABLE II

REACTION OF PHENYL RADICALS WITH PROPYL DISULFIDE AT 60°

PAT, init. molarity × 10²	Final molarities × 10²: $PrSC_6H_5$	C_6H_5H	PrSH	R	Recovery of phenyl radicals, %
10.16	8.50	0.89	0.70	9.55	92
5.08	4.28	.46	.35	9.30	93
1.02	0.89	.09	.03	9.89	96
0.51	0.43	.05	.016	8.60	94
			Av.	9.3 ± 0.3	94

TABLE III

REACTION OF PHENYL RADICALS WITH ISOPROPYL DISULFIDE AT 60°

PAT, init. molarity × 10²	Final molarities × 10²: *i*-$PrSC_6H_5$	C_6H_5H	*i*-PrSH	R	Recovery of phenyl radicals, %
10.11	5.85	3.33	1.16	1.76	91
5.06	2.98	1.70	0.48	1.75	93
1.01	0.58	0.31	.14	1.87	88
0.506	.29	.16	.07	1.81	89
0.101	.07	.04	.05	1.75	109
			Av.	1.79 ± 0.01	94

The thiol is undoubtedly formed by eq. 1a followed by

$$RR'CH—S\cdot + QH \longrightarrow RR'CH—SH + Q\cdot \quad (2)$$

eq. 2 where QH is any hydrogen donor in the system including the disulfide solvent. Since thiols are very active hydrogen donors, they could lead to a spurious amount of benzene being formed. If thiol were responsible for the formation of an appreciable amount of benzene, relatively more benzene would be formed at higher initial concentrations of PAT, since these solutions would contain higher average thiol concentrations. As seen above, R is not a function of PAT concentration. Conclusive proof that the benzene is not formed from thiol is given in the section to follow. There, runs are given in which additional amounts of thiol are added initially; a value of R is obtained by extrapolation to zero concentration of thiol. The value obtained in that way agrees with the values in Tables II and III.

$$RR'CH—SH + C_6H_5\cdot \longrightarrow RR'CH—S\cdot + C_6H_5H \quad (3)$$

The data for the remaining disulfides studied are given in Table IV. Although thiol was qualitatively identified as a product in most of these cases, no attempt was made to analyze quantitatively for it. For these disulfides the value of R also is independent of the initial concentration of PAT.

Effect of Added Thiol on R.—As discussed above, thiols are an ultimate product of the reaction of phenyl radicals with these disulfides, and it is possible that some benzene is formed by reaction of phenyl radicals with thiol rather than with the disulfide solvent. This possibility was eliminated by showing that in the case of propyl and isopropyl disulfides the concentrations of thiol that are formed are too small to affect the amount of benzene formed.

TABLE IV

REACTION OF PHENYL RADICALS WITH DISULFIDES AT 60°

Disulfide	PAT, init. concn. × 10²	Final molarities × 10²: RSC_6H_5	C_6H_5H	R	Recovery of phenyl radicals, %
Methyl	11.94	10.91	0.20	54.6	93
	5.97	5.48	.10	54.8	93
	1.19	1.13	.02	56.5	97
			Av.	55.3 ± 1.1	94
Butyl	10.0	8.17	1.17	7.0	93
	5.00	3.88	0.58	6.7	89
	4.00	3.28	.50	6.6	95
	1.00	0.81	.12	6.7	93
	0.50	0.44	.06	7.3	100
			Av.	6.9 ± 0.09	94
sec-Butyl	10.01	5.35	3.55	1.51	89
	5.00	2.70	1.65	1.64	87
	1.00	0.57	0.32	1.78	89
	0.50	0.28	0.17	1.65	90
			Av.	1.65 ± 0.01	89
Isobutyl	Satd.	7.03	1.08	6.51	...
	5.19	4.12	0.60	6.87	91
	2.60	2.08	.29	7.17	91
	0.52	0.38	.06	6.33	85
	0.26	0.23	.035	6.71	104
			Av.	6.72 ± 0.11	93
t-Butyl	4.93	1.91	2.06	0.93	81
	2.46	0.96	1.01	.95	80
	1.97	.72	0.76	.95	75
	0.99	.40	.42	.95	83
	0.49	.20	.21	.95	84
			Av.	0.95 ± 0.00	81

Table V gives data for the reaction of phenyl radicals with isopropyl disulfide in the presence of varying amounts of added 2-propanethiol. The concentration of PAT is 10.0×10^{-2} M in all of these runs. The data show that added thiol does increase the amount of benzene formed and lead to a lower value of R. However, at concentrations of thiol near those produced by the reaction, the value of R is close to that obtained from

(26) The half-life of PAT at 60° is 23 minutes, and its rate of decomposition is insensitive to the nature of the solvent. See ref. 22, 23a, 23c; S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **75**, 5504 (1953); J. F. Garst and G. S. Hammond, *J. Org. Chem.*, **23**, 98 (1958); R. Huisgen and H. Nakaten, *Ann.*, **586**, 70 (1954).

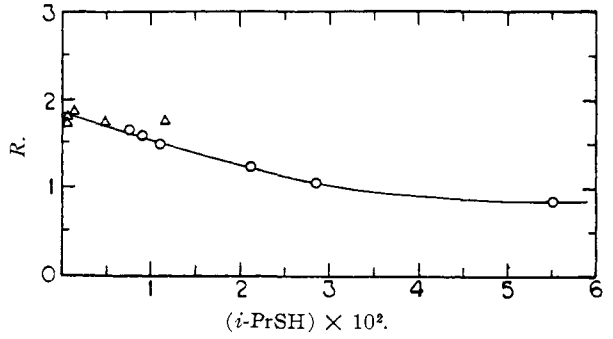

Fig. 1.—Concentration of 2-propanethiol (moles/liter × 10²) *vs.* mole ratio of isopropyl phenyl sulfide to benzene: Δ, no added thiol; O, added thiol.

the data of Table III. Figure 1 shows these data graphically: the value of R is plotted *vs.* the final concentration of thiol. The points for runs in which thiol was added (open circles) extrapolate to give a value of R at zero concentration of thiol that agrees closely with the value obtained from points in which no additional thiol is added (triangles).

TABLE V

REACTION OF PHENYL RADICALS WITH ISOPROPYL DISULFIDE IN THE PRESENCE OF ADDED 2-PROPANETHIOL[a]

Molarities × 10²					Recovery of phenyl radicals, %
i-PrSH					
Initial	Final	C_6H_6H	i-PrSH	R	
10.6	5.51	4.28	3.64	0.85	..
5.31	2.85	4.67	4.95	1.06	96
3.19	2.12	4.16	5.15	1.24	93
2.12	1.10	3.80	5.65	1.49	94
1.06	0.90	3.69	5.88	1.59	95
0.53	0.76	3.61	6.00	1.66	96
0.00	1.15	3.30	5.79	1.75	96

[a] The initial concentration of PAT is 10.0 × 10^{-2} M.

The same is true for propyl disulfide. Table VI gives the data and Fig. 2 is a graph of the final thiol concentration *vs.* R. The value of R extrapolated to zero thiol concentration, 9.4, agrees very closely with that obtained from the data in Table II, namely 9.3.

TABLE VI

REACTION OF PHENYL RADICALS WITH PROPYL DISULFIDE IN THE PRESENCE OF ADDED PROPANETHIOL[a]

Molarities × 10²					Recovery of phenyl radicals, %
PrSH					
Initial	Final	C_6H_6H	$PrSC_6H_5$	R	
10.98	7.53	2.40	7.32	3.05	96
5.49	3.87	1.73	8.21	4.75	99
3.29	2.72	1.50	8.37	5.58	98
2.20	2.22	1.36	8.66	6.37	99
1.10	1.55	1.23	8.71	7.08	99
0.55	0.94	1.11	8.82	7.95	99
0.00	0.75	1.06	8.80	8.30	98

[a] Initial concentration of PAT is 10.0 × 10^{-2} M.

Notice that eq. 1a and 3 result in a steady state in thiol concentration. In some of the runs in Tables V and VI, the final thiol concentration is higher than the initial, and in some the reverse is true.

Table VII summarizes the data. The percentage of the attack by the phenyl radical which occurs on sulfur is given for each disulfide, and is found to decrease smoothly from methyl to *t*-butyl disulfide. The percentage recovery of phenyl radicals is also given, calculated from the moles of benzene and phenyl alkyl sulfide produced per mole of PAT used. This percentage recovery of phenyl radicals is equal to the efficiency of

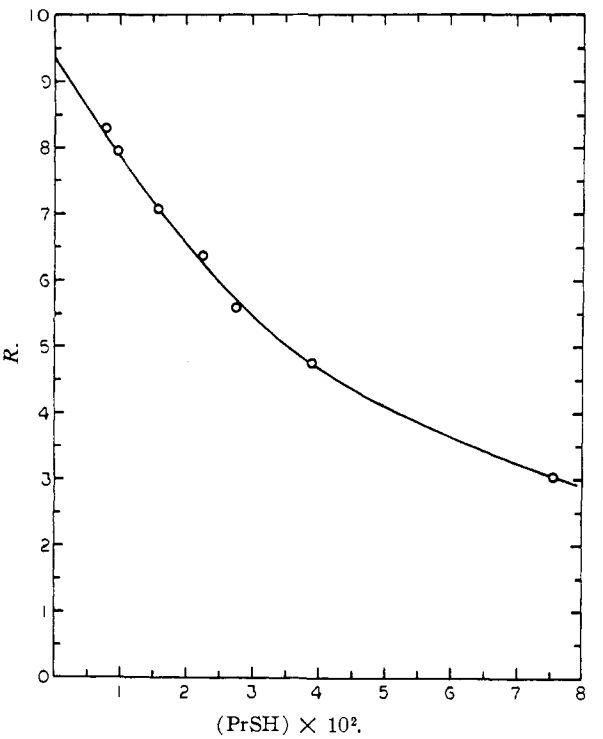

Fig. 2.—Concentration of propanethiol (moles/liter × 10²) *vs.* mole ratio of phenyl propyl sulfide to benzene.

production of free phenyl radicals from PAT if products other than those measured here can be ignored (*e.g.*, biphenyl). In the presence of thiols (Tables V and VI), the efficiency is 96–98%. Thus, products other than benzene and phenyl alkyl sulfide are insignificant in the presence of a good hydrogen donor. Similarly, the efficiency is 94% with methyl disulfide. These data again indicate that the phenyl radicals react almost exclusively with the disulfide solvent. The apparent efficiency decreases to 81% for *t*-butyl disulfide. This is probably due to the fact that the total rate of reaction is slower for this disulfide and the phenyl radicals have a longer average lifetime and form termination-type products to a larger extent.

TABLE VII

PERCENTAGE OF THE ATTACK BY PHENYL RADICALS ON DISULFIDES WHICH OCCURS ON SULFUR[a]

Disulfide	Attack on S, %	Apparent efficiency[b]
Methyl	98.2	0.94
Propyl	90.3	.94
Isopropyl	64.1	.94
Butyl	87.3	.94
sec-Butyl	62.2	.89
Isobutyl	87.0	.93
t-Butyl	48.6	.81

[a] % attack = $(R/(1 + R))$ 100. [b] Moles of benzene plus phenyl alkyl sulfide formed per mole of PAT used.

Discussion

Several experiments[27] involving disulfides as transfer agents in polymerization had indicated that radicals reacted with primary alkyl disulfides at least partially by attack on sulfur, as in eq. 1a. The evidence was somewhat ambiguous, however, because of experimental difficulties, and also because the polymeric nature of the products made it impossible to identify discrete monosulfide products, as required by the stoichiometry of eq. 1a. The data of Table VII show conclusively that the phenyl radical attacks disulfides at sulfur, and that this is the favored reaction for relatively unhindered disul-

(27) These experiments are summarized in ref. 4c, p. 51.

fides. The reasonable supposition[5] is supported that more of the attack is diverted to hydrogen as the sulfur becomes more hindered. This increased fraction of the attack which occurs on the hydrogens of methyl disulfide, for example, relative to *t*-butyl disulfide could result from two factors: Either the methyl hydrogens are attacked faster than are the *t*-butyl hydrogens, or the more hindered *t*-butyl sulfur atom is attacked more slowly. It is possible that both these factors contribute to the observed pattern, but the latter probably is dominant. The *total rate* of attack by the polystyryl radical on *t*-butyl disulfide is 66-fold slower than on methyl disulfide,[5] and the relative rates of attack on the two sulfur atoms will be even more divergent. The reactivity patterns of the phenyl and the polystyryl radicals toward disulfides are probably parallel.

Reactivity of the Phenyl Radical.—The data of Tables V and VI can be used to calculate the reactivity of the phenyl radical with thiols relative to disulfides, k_3/k_1. If it is assumed that all of the additional benzene formed when thiol is present comes from eq. 3, then the rate of eq. 3, R_3, is equal to the benzene formed in the presence of thiol less that formed in its absence. The rate of eq. 1, R_1, is the sum of the phenyl alkyl sulfide produced plus the benzene formed in the absence of thiol.

$$\frac{R_3}{R_1} = \frac{k_3(C_6H_5\cdot)(RSH)}{k_1(C_6H_5\cdot)(R_2S_2)} \cong \frac{\text{extra benzene formed in presence of thiol}}{RSC_6H_5 + \text{benzene formed in the absence of thiol}}$$

Thus

$$\frac{k_3}{k_1} = \left[\frac{\text{extra benzene formed}}{RSC_6H_5 + \text{benzene}}\right] \frac{(R_2S_2)}{(RSH)}$$

where (R_2S_2) is the molarity of the disulfide solvent and (RSH) is the average molarity of the thiol taken from Tables V and VI.

Table VIII gives the data, and the relative constancy of k_3/k_1 justifies the assumptions. Thus, the phenyl radical reacts with 2-propanethiol 23-fold faster than it reacts with isopropyl disulfide, and it reacts with propanethiol 8-fold faster than with propyl disulfide. These values may be compared with comparable values for the polystyryl radical. For the polystyryl radical, k_3/k_1 equals the transfer constant for the thiol divided by that for the analogous disulfide.[28a] The transfer constant of 2-propanethiol at 60° in styrene is 3.1 as determined by Morton,[29] and that of isopropyl disulfide is[5,28b] 6.6×10^{-4}. The transfer constant[28b] of propanethiol has not been measured, but butanethiol, which should be similar, has a transfer constant equal to 22; the transfer constant of propyl disulfide is 23×10^{-4}. Thus, the polystyryl radical reacts with 2-propanethiol 5000-fold faster than it reacts with isopropyl disulfide, and it reacts with propanethiol about 10^4 times faster than with propyl disulfide. The polystyryl radical, therefore, is enormously more selective than is the phenyl radical, but its reactivity pattern toward disulfides and thiols parallels that of the phenyl radical. The relative reactivity of these radicals toward toluene (relatively non-polar) and carbon tetrachloride (of similar polarity to a disulfide) is relevant.[30] The polystyryl radical reacts 0.0014 times as fast with toluene as with carbon tetrachloride,[4b] the methyl radical 0.75 times as fast,[9] and the phenyl radical 0.4 times as fast.[24] Again, the polystyryl radical is more selective, but its reactivity parallels that of the phenyl radical.

TABLE VIII

RELATIVE REACTIVITIES OF PHENYL RADICAL WITH THIOLS AND DISULFIDES at 60°

Isopropyl disulfide[a]		Propyl disulfide[b]	
(RSH) × 10², av.	k_3/k_1	(RSH) × 10², av.	k_3/k_1
8.06	10.9	9.26	10.8
4.08	25.3	4.68	9.8
2.66	23.8	3.01	9.8
1.61	21.6	2.21	8.8
0.98	27.0	1.33	7.3
0.65	31.9	0.75	4.3
	Av. 23		Av. 8.5

[a] Benzene in excess of 3.30×10^{-2} *M* is assumed to arise from reaction 3. All other products are assumed to be from reaction 1; data of Table V; disulfide molarity is 6.2 *M* at 30°, the reference temperature. [b] Benzene in excess of 1.06×10^{-2} *M* is assumed to arise from reaction 3; data of Table VI; disulfide molarity is 6.3 at 30°.

Knowledge of the total rate of attack by phenyl radicals on the disulfides studies here will permit use of reaction 1 as a model for the bimolecular radical displacement reaction.[4c,5] A study aimed at obtaining these data is underway in this Laboratory using the Edwards and Mayo technique.

After the study reported here was completed, a paper by Suama and Takezaki[31] appeared in which the rate constant for reaction of methyl radicals with methyl disulfide was measured. These workers photolyzed azomethane in the gas phase at 100° in the presence of methyl disulfide and analyzed the products by g.p.c. They obtained both methyl sulfide and methane as products, corresponding to reactions 1a and 1b. The product ratios lead to the conclusion that 78% of the attack occurs on sulfur. Again, the methyl radical is less selective than is the phenyl; however, a higher temperature and reaction in the gas phase also would be expected to decrease selectivity. A further comparison can be made using these data. The Japanese workers are able to measure k_1 relative to the rate of dimerization of methyl radicals, k_m. They obtain $k_1/k_m = 3 \times 10^{-6}$. The absolute value of k_m can be approximated from the work of Gomer and Kistiakowsky,[32] and is approximately 2×10^{10} l. mole^{-1} sec.$^{-1}$ at 100°. Thus, the absolute value of the rate constant for the reaction of methyl radicals with methyl disulfide at 100° in the gas phase is 6×10^4 l. mole^{-1} sec.$^{-1}$. The rate constant[2a] for the reaction of polystyryl radicals with methyl disulfide is about 1.4 l. mole^{-1} sec.$^{-1}$ at 60° and about 4 l. mole^{-1} sec.$^{-1}$ at 100°. Thus, methyl radicals react some 10^4 times faster than do polystyryl radicals.

(28) Reference 4c; (a) p. 52, (b) pp. 53, 84.

(29) M. Morton, J. A. Cala and J. Piirma, *J. Am. Chem. Soc.*, **78**, 5394 (1956).

(30) See the general treatment of radical reactivities in: C. H. Bamford, A. D. Jenkins and R. Johnston, *Trans. Faraday Soc.*, **55**, 418 (1959).

(31) M. Suama and Y. Takezaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, (Japan), **40**, 229 (1962).

(32) R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951); *e.g.*, see, G. O. Pritchard, H. O. Pritchard and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1425 (1954).