Kinetics of the Thermal Decompositions of Diaryl and Dialkyl Disulfides

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A kinetic study of the thermal decomposition of diphenyl disulfide, its *p*-methoxy, *p*-methyl, and *p*-chloro derivatives, and di-*n*-butyl and di-*t*-butyl disulfides in tetralin was made. The rate of decomposition was followed by the decrease of disulfide and the spontaneous first-order rate constants for these disulfides at 196, 207, and 217 °C and the activation parameters were obtained. It was observed that the rates of the decompositions for diaryl disulfides are increased by *p*-substituents ($CH_3O > Cl \simeq CH_3 > H$) and that that of di-*t*-butyl disulfide is comparable to diaryl disulfides, whereas, di-*n*-butyl disulfide shows no decomposition under these conditions. A reaction scheme of the decomposition including induced decomposition is proposed from the kinetic results and product analysis. Moreover, the properties of a thiyl radical in relation to the above results are discussed from the electronic and ESR spectra of the aryl thiyl radicals generated from the photolysis of corresponding thiols in a glass of 2-methyltetrahydrofuran at −196 °C.

Although it is well known that the S—S bonds in organic disulfides are cleaved homolytically by heat or light yielding thiyl radicals,[1] there are few kinetic studies of the thermal decomposition of organic disulfides. The dissociation of tetramethylthiuram (TMTD) and 2,2′-dibenzothiazolyl (DBTD) disulfides into their thiyl radicals has been demonstrated from magnetic measurements[2] and these radicals initiate the radical polymerization of styrene and methyl methacrylate (MMA)[3,4] at temperatures above 60 °C. The first-order rate constants for the decomposition of TMTD at two temperatures (60 °C and 80 °C) have been estimated by Ferington and Tobolsky[3] from kinetic studies of styrene and MMA polymerizations initiated by the disulfide, and Davis and Perrin[5] have also determined the rate constants for both TMTD and DBTD at 56 °C and 100 °C using diphenylpicrylhydrazyl (DPPH) as a scavenger for radicals formed thermally. However, for both diaryl and dialkyl disulfides the first-order rate constants have so far not been reported, though the formation of thiyl radicals from the homolytic scission of disulfides has already been indicated from the fact that the reaction of diphenyl disulfide with benzyl alcohol gives both aldehyde and thiophenol[6] and that such a disulfide dehydrogenates from hydrocarbons.[7,8] Leandri and Tundo[9] have investigated the effects of substituents on the extent of the decomposition of diaryl disulfides at 170 °C from molecular weight measurements, but they have not determined the rate constants.

The purpose of this paper is to determine the first-order rate constants for the thermal decompositions of some symmetric diaryl and dialkyl disulfides in tetralin, and to obtain a relationship between the structure and the susceptibility to decomposition, as well as other information about the properties of thiyl radicals.

Experimental

Materials. Commercially available, diphenyl, di-*t*-butyl, and di-*n*-butyl disulfides were recrystallized three times from ethanol. Di-*p*-chlorophenyl and di-*p*-methylphenyl disulfides were prepared from the oxidations of the corresponding thiols and recrystallized from ethanol. Di-*p*-methoxyphenyl disulfide was prepared by the method of Tarbell and Fukushima[10] and recrystallized three times from ethanol. Tetralin was washed successively with concentrated sulfuric acid, water, 10% aqueous sodium carbonate, water, and then dried over anhydrous sodium sulfate and distilled from sodium metals. The distillate was refluxed over DPPH and redistilled before use.

Kinetics. A weighed sample of disulfide was dissolved in a known volume of tetralin. The solution was placed in a Pyrex glass-reaction tube, degassed many times (usually 6—9 times) by the freeze-thaw method, and finally the reaction tube was filled with nitrogen, sealed off and immersed in an oil bath which was maintained at the desired temperature to within ±0.1 °C. An aliquot of the solution was withdrawn after a definite time interval into a sample tube attached to the reaction tube, and evacuated by a high-vacuum pump through a stopcock. Then, the quantity of residual disulfide in the aliquot was determined by the following method:[11] the disulfide in the aliquot was reduced to the corresponding thiol with sodium borohydride and aluminum chloride and the quantity of the resulting thiol was determined by titration with silver nitrate using dithizone as an indicator.[12] Since the reaction mixture contained the thiol formed from the hydrogen abstraction of the thiyl radical, the disulfide content was determined by subtracting the amount of thiol in an unreduced aliquot from that obtained after reduction. It has been reported that the thiol and sulfide formed during the decomposition of disulfides (see the following section) are unchanged by the reduction and the presence of these compounds does not interfere with the reduction and titration.[11] The preliminary experiments show that the accuracy of the titration for diphenyl, di-*p*-methoxyphenyl, di-*p*-methylphenyl, di-*p*-chlorophenyl, and di-*n*-butyl disulfides is 99.0—99.5, 99.2—99.7, 93.0—93.5, and 98.5—99.0%, respectively.

The rate of decomposition is known to be represented generally by the following equations,[15]

$$-\mathrm{d}[\mathrm{P}]/\mathrm{d}t = k_1[\mathrm{P}] + k_i[\mathrm{P}]^n = k_{\mathrm{obsd}}[\mathrm{P}] \qquad (1)$$

$$k_{\mathrm{obsd}} = k_1 + k_i[\mathrm{P}]^{n-1} \qquad (2)$$

where [P] is the concentration of the decomposed substance (disulfide, in this case) and k_1 and k_i are the first-order (spontaneous) rate constant and a constant including the rate constant for induced decomposition, respectively. The apparent first-order rate constants for various initial concentrations of disulfide were obtained from the slopes in the first-order plots (line (a) in Fig. 1) in a region of low conversion ($[\mathrm{P}] \simeq [\mathrm{P}]_0$), and then, these were treated according to Eq. (2) in order to obtain k_1 and n, as will be described in the section on the Results. In our experiments, first-order plots gave straight lines to at least a 20% conversion.

Analysis of Products for a Large Scale Experiment. A solution of 4.36 g (0.02 mol) of diphenyl disulfide in 70 ml of tetralin was deaerated with nitrogen gas and allowed to react at a reflux temperature (270.2 °C) for 90 hr. Most of the tetralin and thiophenol were distilled from the reaction mixture and then 1.32 g (0.012 mol) of thiophenol was isolated as a yellow crystal of lead salt (I) by the reaction of thiophenol with lead acetate.[13] This yield of thiophenol was almost equal to that obtained by titration with silver nitrate.

Found: C, 34.07; H, 2.16%. Calcd for $C_{12}H_{10}PbS_2$ (I): C, 33.86; H, 2.35%.

The residual mixture was analyzed by chromatography on a silica gel column in the usual way. Elution with petroleum ether gave tetralin, and then using a 90: 10 petroleum ether–benzene mixture, unreacted diphenyl disulfide (0.006 mol, 1.3 g). The oily product was eluted with a 80: 20 petroleum ether–benzene mixture and identified as 1,2,3,4-tetrahydro-1-phenylthionaphthalene (II) (0.006 mol, 1.4 g): NMR (δ, CCl_4): 4.45 (1H, t, CH), 1.6—2.0 (4H, m, CH_2), 2.4—2.8 (2H, m, $-CH_2-C_6H_4-$), 6.9—7.4 ppm (9H, m, arom).

Found: C, 80.76; H, 7.11; S, 14.00%. Calcd for $C_{16}H_{16}S$ (II): C, 79.95; H, 6.71; S, 13.34%. The yellow oily fraction (about 0.3 g) containing both sulfur (14.2%) and tetralin fragments was eluted with a 50: 50 petroleum ether–benzene mixture. Elution with diethyl ether produced a brown oily fraction (about 0.4 g) containing sulfur (6.9%) and tetralin fragments. The formation of a small amount of naphthalene was observed using glc.

Spectra of Thiyl Radicals. The electronic spectra of aryl thiyl radicals generated by the photolysis of the corresponding thiols in a rigid glass of 2-methyltetrahydrofuran (2-MTHF) at liquid nitrogen temperature have been obtained (matrix isolation technique[14]). The concentration of each thiol was 0.01 mol/l and a super-high-pressure mercury lamp was used for the photolysis.

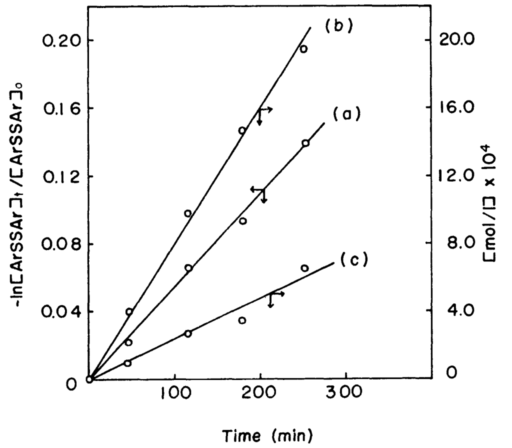


Fig. 1. (a) Plot of the first-order kinetics for the decomposition of di-*p*-methoxyphenyl disulfide (0.010 M) at 207 °C. (b) Rate of thiol formation determined by the titration with silver nitrate. (c) Rate of "other product" formation estimated from the subtraction of the rate of thiol formation from that of di-*p*-methoxyphenyl disulfide decomposition.

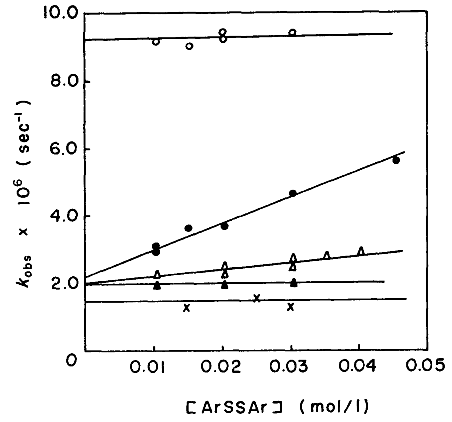


Fig. 2. Plots of k_{obs} *vs.* the concentration of disulfide at 207 °C: (×) diphenyl disulfide; (●) di-*p*-chlorophenyl disulfide; (○) di-*p*-methoxyphenyl disulfide; (△) di-*p*-methylphenyl disulfide; (▲) di-*tert*-butyl disulfide.

Results

Kinetics. The thermal decompositions of various disulfides were studied in tetralin which is a good hydrogen-donating compound. In Fig. 2 (n=2 in Eqs. 1 and 2), the apparent first-order rate constants (k_{obsd}) for various initial concentrations are plotted against the initial concentrations of the disulfides. Nozaki and Bartlett[15] have indicated in their studies on the decomposition of the substituted benzoyl peroxides that the order n of the induced decomposition in Eq. (1) (and Eq. 2) can vary between 0.5 and 2.0, depending on which radicals attack the parent molecules and on the type of radicals participating in the termination step. In our experiments the

Table 1. First-order rate constants and activation parameters for the thermal decomposition of diaryl and dialkyl disulfides in tetralin.

Disulfide	Temp. °C	$k_1 \times 10^6$ s^{-1}	ΔS cal mol^{-1}	E_a kcal mol^{-1}
Diphenyl disulfide	196	0.47		
	207	1.1	1.5	43.0
	217	3.3		
Di-*p*-chlorophenyl disulfide	196	0.80		
	207	2.2	−4.0	40.0
	217	5.0		
Di-*p*-methoxyphenyl disulfide	196	3.3		
	207	9.0	0.5	40.6
Di-*p*-methylphenyl disulfide	207	2.0	−5.4	39.4
	217	4.6		
Di-*t*-butyl disulfide	207	1.9[a]		
Di-*n*-butyl disulfide	207	No decomposition[b]		

a) Value estimated from the amount of thiol formed. b) No decomposition occurs at 207°C for 20 hr.

trial and error method for determining n in Eq. (2) gives straight lines with different slopes for di-*p*-chlorophenyl and di-*p*-methylphenyl disulfides when n is equal to 2. Thus, it is suggested that a considerable amount of induced decomposition occurs in the decomposition of di-*p*-chlorophenyl disulfide and probably a small amount in that of di-*p*-methylphenyl disulfide, whereas, for the other disulfides no appreciable concentration effect was observed. The values of k_1 for both di-*p*-chlorophenyl and di-*p*-methylphenyl disulfides were estimated from an extrapolation of the straight lines to zero concentration; these values of k_1 were found to be 0.8×10^{-6}, 2.2×10^{-6}, and $5.0\times10^{-6}\ s^{-1}$ at 196, 207, and 217 °C, respectively. The k_1 values for other disulfides at 196, 207, and 217 °C and the activation parameters are shown in Table 1. Since di-*t*-butyl disulfide was not reduced quantitatively with sodium borohydride, the k_1 value was estimated from the amount of the thiol formed and so this value may be considered to be the lower limit of the true value.

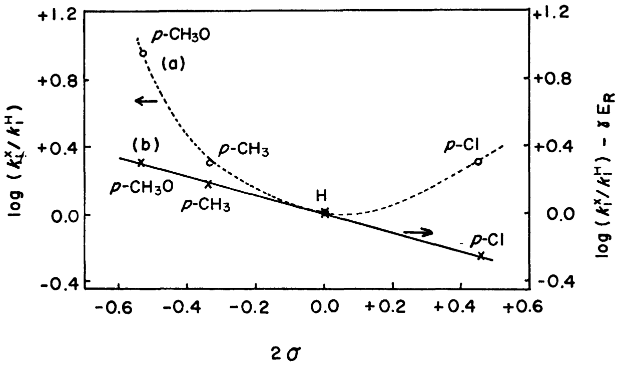


Fig. 3. Hammett plots of the first-order rate constants for the decompositions of di-*p*-substituted phenyl disulfides: (a) Log (k_1^X/k_1^H) *vs.* Hammett's σ values. (b) Log (k_1^X/k_1^H)$-\gamma E_R$ (Yamamoto-Otsu's equation) *vs.* Hammett's σ value ($\rho=-0.55$, $\gamma=3.0$).

The Effects of p-*Substituents on the Values of* k_1. Fig. 3(a) shows a plot of $\log k_1^X/k_1^H$ *vs.* 2σ, where k_1^H and k_1^X are the first-order rate constants for diphenyl and di-*p*-substituted phenyl disulfides, respectively, and σ is the usual Hammett substituents sigma-value. This plot does not give a straight line, but rather a curve which has a minimum value for diphenyl disulfide. The Yamamoto-Otsu equation,[16]

$$\log k_1^X/k_1^H = 2(\rho\sigma+\gamma E_R) \tag{3}$$

which is a modified Hammett equation including the resonance term, was applied to the present data of k_1 (Fig. 3(b)) in which σ and E_R are the polar and resonance substituent constants and ρ and γ are the reaction constants giving the susceptibilities for the polar and resonance effects of the substituents respectively. A constant 2 is used here, since symmetrically-substituted phenyl disulfide has two substituents. As shown in Fig. 3(b), the values of -0.55 and 3.0 for ρ and γ, respectively, are found to give a straight line.

Products Analyses. The rate of formation of the thiol obtained by titration with silver nitrate and that of "products" other than thiol are indicated by (b) and (c), respectively, in Fig. 1. This latter rate was obtained by the subtraction of the rate of the formation of thiol from that of the decomposition of the disulfide, and since these products are not reduced by sodium borohydride and aluminum chloride, they are, therefore, probably aryl sulfide (see Experimental). Fig. 1 indicates that the thermal decomposition of 1 mol of disulfide yielded about 1.5 mol of thiol and 0.5 mol of "other products". The analysis of products obtained from a large scale experiment for diphenyl disulfide at a reflux temperature of tetralin indicates the formation of thiophenol (0.90 mol), 1,2,3,4-tetrahydro-1-phenylthionaphthalene (0.41 mol) per 1 mol of diphenyl disulfide consumed, and unidentified oily products containing sulfur and tetralin fragments. Nakasaki[7] has reported that thiophenol and naphthalene were formed from the decomposition of diphenyl disulfide in tetralin at 260 °C. Ritter and Sharpe[8] have also found a similar dehydrogenation of tetralin by *iso*-amyl disulfide. Both authors have used disulfides as dehydrogenation reagents and thus the concentrations of disulfides in their experiments (11—18 mol/l) are much higher than that in those reported here (0.29 mol/l).

Discussion

Mechanism. The following reactions can be considered as the elementary steps in the thermal decomposition of disulfides in tetralin,

$$\mathrm{ArSSAr} \xrightarrow{k_1} 2\mathrm{ArS}\cdot \tag{4}$$

$$\mathrm{ArS}\cdot + \mathrm{RH} \xrightarrow{k_2} \mathrm{ArSH} + \mathrm{R}\cdot \tag{5}$$

$$\mathrm{ArS}\cdot + \mathrm{R}\cdot \xrightarrow{k_3} \mathrm{ArSR} \tag{6}$$

$$\mathrm{R}\cdot + \mathrm{R}\cdot \xrightarrow{k_4} \text{product} \tag{7}$$

$$\mathrm{ArS}\cdot + \mathrm{ArSSAr} \xrightarrow{k_5} \mathrm{ArS}\cdot + \text{product} \tag{8}$$

$$\mathrm{R}\cdot + \mathrm{ArSSAr} \xrightarrow{k_6} \mathrm{ArS}\cdot + \text{product} \tag{9}$$

where RH and R· are tetralin and its derived radical, respectively. A thiyl radical (ArS·) formed from step 4 abstracts α-hydrogen from tetralin (step 5) and the tetralinyl radical thus formed terminates with a thiyl radical or other tetralinyl radical. The step involving the addition of a thiyl radical to a phenyl ring is ignored since no such product was obtained.

Pryor, Gojon, and Stanley[17] have reported that the self-termination of the thinyl radicals is the only significant termination reaction in the reaction of the cyclohexyl thiyl radical with cumene at 80 °C. However, the reverse reaction of step 4 (self-termination) outside of the solvent-cage was ignored because of the situation described below. Probably due to the greater stability of the phenyl thiyl radical compared to that of the cyclohexyl thiyl radical, our preliminary experiment on the flash photolysis of *p*-chlorothiophenol in tetralin at room temperature[18] shows that the decay of the *p*-chlorophenyl thiyl radical obeyed first-order kinetics, that is, the thiyl radical reacts with tetralin and not with each other (the rate constant for this hydrogen abstraction reaction by the thiyl radical being found to be 1.5×10^2 $M^{-1}s^{-1}$), whereas, in a cyclohexane solution the thiyl radical decayed with second-order kinetics, indicating the self-termination of the thiyl radicals (the rate constant for the self-termination reaction was $2k_t=1.2\times10^9$

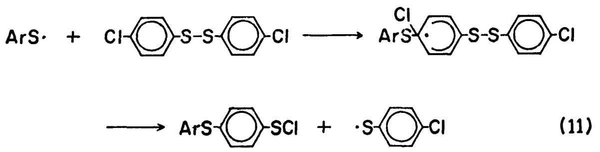
M^{-1} s^{-1}, this value being consistent with that of Thyrion[19]). Since the activation energy for hydrogen abstraction may be greater than that for a coupling reaction, these results can be used to consider our reaction scheme (our decomposition experiments were conducted at much higher temperatures than those on flash photolysis), and the rate constants obtained here are the values extrapolated to zero concentration of the disulfides, *i.e.*, they were obtained in extremely unfavorable conditions for the self-termination of thiyl radicals.

The k_{obsd} obtained in the decomposition of diphenyl and di-*p*-methoxyphenyl disulfides hardly varied with the initial concentrations of the disulfides, and these results are expected for the two following cases: (1) for $k_{obsd}=k_1$, and (2) for $k_{obsd}=k_1+k_i$, which is derived from $n=1.0$ in Eq. (1) (that is, in this case the decomposition proceeds by steps 4, 5, 6, and 9). The contribution of induced decomposition to k_{obsd}, such as in the second case, can be excluded experimentally by the presence of radical scavengers (a stable radical is used in these experiments), but this common method of using a stable free radical could not be applied at these high temperatures. For the following reasons, however, the process consisting of steps 4, 5, 6, and 9 leading to $n=1.0$ in Eq. (1) (and Eq. 2) can be neglected. First, as shown in Fig. 1, about 1.5 mol of the thiol (hydrogen abstraction product from tetralin by the thiyl radical) were obtained per mol of disulfide consumed. If a considerable amount of induced decomposition for $n=1$ occurs, the thiol yield should be less than 1 mol from steps 6 and 9. The yield (1.5 mol) greater than 1 mol indicates that all or a large portion of the thiyl radical was formed by step 4 (the maximum value being 2 mol when the termination occurs only due to step 7 which may not be the case from the fact that ArSR (product from step 6) was formed with a considerable yield). Second, step 9 is the attack of the disulfide by the tetralinyl radical. Tsuda and Otsu[20]) have reported that a kinetic study of the induced decomposition of di-*p*-substituted phenyl disulfides with the polystyryl radical (the same benzyl-type radical as the tetralinyl radical) resulted in $+0.23$ for ρ in the Yamamoto-Otsu equation. Thus, if step 9 occurs at a high rate, the present ρ value should be a positive value, however, it is found to be -0.55. Moreover, the results reported by Nakasaki[7]) and Ritter and Sharpe[8]) suggest that the tetralinyl radical does not attack the disulfide, unlike the case of the reactive phenyl radical.[21]) Therefore, the thermal decompositions of diphenyl and di-*p*-methoxyphenyl disulfides, for which the induced decomposition is found to be negligibly small, as shown in Fig. 2, seem to proceed *via* a process consisting of steps 4, 5, 6, and 7.

Steps 8 and 9 are considered to be induced decompositions by thiyl and tetralinyl radicals, respectively, which may occur in the thermal decomposition of both di-*p*-chlorophenyl and di-*p*-methylphenyl disulfides. The kinetic equation of the decomposition, assuming step 9 to be an induced decomposition, is not consistent with the present data, because the order n in Eq. (1) is not 2.0. However, if step 8 is assumed, the order n is 2.0, regardless of the type of termination step (step 6 or 7), in agreement with the present experimental results. From steps 4, 5, 6, and 8, the following equation can be derived:

$$-\frac{\mathrm{d}[\mathrm{ArSSAr}]}{\mathrm{d}t} = k_1[\mathrm{ArSSAr}] + \frac{k_1k_5[\mathrm{ArSSAr}]^2}{k_2[\mathrm{RH}]} \qquad (10)$$

It appears reasonable that the thiyl radical induces the decomposition, while the tetralinyl radical does not, and thus, the latter radical may be more stable and less reactive than the thiyl radical. If induced decomposition by the tetralinyl radical under the present experimental conditions (high temperature and low disulfide concentration) occurs in a manner similar to that in the case of the polystyryl radical for the disulfide as previously described, di-*p*-methoxyphenyl disulfide should also be susceptible to induced decomposition. Benati and his coworkers[22]) have reported interesting reactions of the thiyl radical with halogenobenzene; the phenyl thiyl radical formed from the homolytic scission of diphenyl disulfide in halogenobenzene attacks the carbon being substituting for the halogen atom and produces phenyl sulfide. From this result, reaction (11) is speculated to be the reaction of the thiyl radical with di-*p*-chlorophenyl disulfide.



(11)

Rate Constants and Activation Parameters. Table 1 shows that the homolytic scission of S—S bonds in disulfides is more difficult than of O–O bonds in peroxides for which the bond dissociation energy is 34—37 kcal/mol for diaryl peroxides and nearly 30 kcal/mol for dibenzoyl peroxide.[23]) Although, from thermochemical studies, the bond energies of S–S bonds in dialkyl and diphenyl disulfides (in gas phase) are calculated to be 67—68[24]) and 64 kcal/mol,[25]) respectively, the bond dissociation energies of S–S bonds obtained experimentally for polysulfides (*e.g.*, dimethyltetrasulfide and S_8 ring), TMTD, DBTD, and benzhydrylhydro disulfide in solution are 36,[26]) 31.6,[3]) 26,[5]) and 20 kcal/mol,[27]) respectively, which are comparable to those of the O–O bonds in peroxides. Thus, the activation energies obtained (39.4—43.0 kcal/mol) for the decomposition of diaryl disulfides are reasonable values.

The Effects of Structure on the Decomposition. The following results suggest that the stability of thiyl radicals formed from decomposition is an important factor in the decomposition of the disulfide; the homolytic scission of S–S bonds in diaryl disulfides is easier than that of S–S bonds in dialkyl disulfides (for example, compare with di-*n*-butyl disulfide in Table 1). This can be explained from the greater stability (resonance stabilization) of aryl thiyl radicals in comparison with that of alkyl thiyl radicals.[28]) The rates of the decompositions of the di-*p*-substituted phenyl disulfides are increased by a *p*-substituent, and the order of decreasing rates is $CH_3O > Cl \simeq CH_3 > H$. This order might be expected from the stability of thiyl radicals, which is increased by the resonance interaction of the *p*-substituent with the aromatic ring.[29]) Similar curves for the Hammett plots have also been obtained for the decompositions of substituted benzoyl peroxides in acetophenone,[30]) the dissociation of hexaaryl ethane into triaryl methyl radicals,[31] and some substituent effects on the free-radical properties such as the $\lambda_{\max}$ shift in the electronic spectra of some nitrogen-centered radicals.[32]

It has been reported that, in the thermal decomposition of di-*p*-substituted benzoyl peroxides and of peresters, electron-donating substituents increase the rate of decomposition, since these substituents increase the difference in the electronegativity between the peroxide oxygens and the aromatic ring, and the repulsion between the negative charges located on the peroxide oxygen destabilizes the parent molecule in the ground state of the decomposition. Thus, the ρ value is negative in the Hammett equation, whereas, peroxides having electron-attracting substituents are subject to induced decomposition, with the ρ value being positive.[33] In the present study the ρ value (-0.55) in the Yamamoto-Otsu equation is also negative (the value of γ is 3.0), that is, electron-donating substituents destabilize the disulfide and increase the rate of thermal decomposition, probably for the same reason as that in the case of peroxides. It is interesting that the rate of decomposition of di-*t*-butyl disulfide is high and comparable to that of diaryl disulfides, whereas, di-*n*-butyl disulfide did not decompose under the same conditions. In the decomposition of dialkyl peroxides, however, it has been reported[34] that di-*t*-butyl and diethyl peroxides have the same dissociation energy. Therefore, the high reactivity of di-*t*-butyl disulfide, which is less strained than di-*t*-butyl peroxide, cannot be explained in terms of strain.

It may be concluded from the present study that *p*-substituents in di-*p*-substituted phenyl disulfides influence both the destabilization of the disulfide and the stabilization of the thiyl radical formed from thermal decomposition, and these two factors accelerate the rate of thermal decomposition of the disulfides.

TABLE 2. $\lambda_{\max}$ IN THE ELECTRONIC SPECTRA OF ARYL THIYL RADICALS IN 2-MTHF AT -196 °C AND OF BENZYL-TYPE RADICALS

Radical		$\lambda_{\max}$ (nm)	
p-Methoxyphenyl thiyl[a]		410 (418)[b]	530
p-Methylphenyl thiyl	312	397 (396)[b]	513
p-Chlorophenyl thiyl	318	386 (381)[b]	516
Phenyl thiyl	308	390 (387)[b]	
Benzyl[c]	318	452	
Phenoxy[d]	300	403	
Anilino[e]	307	400	

a) Value obtained from the photolysis of di-*p*-methoxyphenyl disulfide. b) Ref. 14(b). c) Ref. 35(a). d) Ref. 35(b). e) Ref. 35(c).

Electronic Spectra of Aryl Thiyl Radicals. Electronic spectra of *p*-substituted phenyl thiyl radicals were observed by the photolysis of the thiols in a 77 K-matrix of 2-MTHF in order to obtain some information about the electronic states of aryl thiyl radicals and the interaction between the *p*-substituent and the odd electron of the radical. The absorption maxima of aryl thiyl radicals are summarized in Table 2 together with other benzyl-type radicals such as benzyl, phenoxy, and anilino radicals. Table 2 shows that the absorption maxima of phenyl thiyl radical at 310 and 390 nm are shifted by the *p*-substituents (the ESR spectrum of the phenyl thiyl radical being characterized by a large anisotropic g value ($g_{/\!/}=2.020$ and $g_{\perp}=2.019$) under the same conditions). Similar absorption maxima around 300 and 400 nm being assigned to the π-electronic spectra of benzyl, phenoxy, and anilino radicals, the shift of the absorption maxima due to substituents have been observed by Porter and his co-workers,[35] and the molecular orbitals of the radicals have been calculated theoretically.[36] A comparison with the position of the absorption maxima of benzyl-type radicals and the considerable change in position due to *p*-substituents suggest that the thiyl radicals should be π-type radicals, which is supported by some theoretical and ESR studies,[37] and the present kinetic results, suggesting the importance of the conjugation among the sulfur atom, the phenyl ring, and the *p*-substituent.

Finally, it is found from a comparison of the first-order rate constants at 207 °C calculated from activation parameters taken from the literature[38] (Table 3), that the homolytic scission of S–S bonds in disulfides is most improbable in comparison with such related compounds as $\mathrm{Ar}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\text{–}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{Ar}$, $\mathrm{Ar}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\text{–}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{Ar}$, $\mathrm{Ar}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\text{–}\mathrm{SAr}$, $\mathrm{Ar}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\text{–}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{Ar}$, and $\mathrm{Ar}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\text{–}\mathrm{SAr}$, which differ in the oxidation state of the sulfur atom in the S–S bonds. Kice[39] has explained the change in the rate of the homolytic scission of these compounds by the difference in the stability of the radicals, stating that $\mathrm{ArSO}\cdot$ is more stable than either $\mathrm{ArS}\cdot$ or $\mathrm{ArSO_2}\cdot$.

We would like to thank Dr. K. Kikuchi and Dr. O. Ito for helpful discussions concerning the spectroscopic studies.

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TABLE 3. EASE OF HOMOLYTIC DISSOCIATION FOR VARIOUS S–S BONDS AT 207 °C

Compd.	$\mathrm{Ar{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{{-}Ar}$[a]	$\mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{{-}Ar}$[b]	$\mathrm{Ar{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{{-}S{-}Ar}$[c]	$\mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}Ar}$[e]	$\mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}S{-}Ar}$	$\mathrm{Ar{-}S{-}S{-}Ar}$[e]
$k_1\ \mathrm{s^{-1}}$	Very large	7.6×10^{2}	3.4	1×10^{-2}	—	$(1—9)\times10^{-6}$

a) Ref. 38(c). b) Ref. 38(a). c) Ref. 38(b). d) Ref. 38(c). e) This work.

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