

Figure 3. Plot of the integrated rate expression, eq IV: circles, experimental data from experiment 10; solid line, theoretical computation using Treanor-Runge-Kutta method (see text).

ample, this trend has also been observed in the decomposition of the triatomic NF_2^7 and the tetratomic C_2N_2 .¹⁶ Although a decrease in activation energy in the secondorder region is predicted by all theories of unimolecular reactions, the energy difference in these cases is larger than can be accounted for by these theories.

For example, when the NF₃ bimolecular rate constants are fitted to the classical collision theory expression in the form¹⁷

$$k_{\rm M} = [PZT^{1/2}/(n/2)!](E_0/RT)^{n/2} \exp(-E_0/RT)$$

with a critical energy of $E_0 \simeq 57$ kcal mol⁻¹, a value of n = 24 is obtained for the number of square terms of internal energy effective in dissociation which exceeds the theoretical maximum value of 15. Alternatively, with n = 15the predicted dissociation energy is found to be 46 kcal mol^{-1} which is too low to be attributed to experimental error.

In a recent paper by Kiefer,¹⁴ similarly low apparent activation energies in diatomic molecules were treated theoretically. His results indicated that the apparent low activation energy can be attributed to the effect of vibrational to vibrational energy transfer which causes a serious depression in the rate at high temperatures and a slight increase in the rate at low temperatures. It was also pointed out that such intermolecular relaxation processes could account for low apparent activation energies in small polyatomic molecules. However, a theoretical treatment does not appear feasible at present, since the participation of the additional vibrational modes greatly complicates the problem.

It is, therefore, concluded that the observed apparent activation energy bears no direct relation to any theoretical thermochemical quantity but is to be viewed strictly as an empirical kinetic parameter, which is useful in describing the dissociation of small molecules.

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Flash Photolysis of Aromatic Sulfur Molecules¹

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A transient absorption spectrum with a maximum at 297 nm and a continuous band up to 520 nm has been observed after flash photolysis of thiophenol and unsubstituted sulfides in solution and has been attributed to the phenylsulfur radical. Substituted sulfides show similar transients with a shift to longer wavelengths. Sulfoxides displayed a spectrum with a short wavelength band at 312 nm. Absorption spectra of the triplet states of thionaphthene, dibenzothiophene, thioxanthene, and thianthrene have been recorded. Kinetic studies of the radicals reactivity and triplet decay are described.

Many attempts to detect organic sulfur radicals have been already reported.³ Some of them were based on determinations of molecular weight, light absorption, and magnetism by the monovalent sulfur radicals after thermal or photochemical dissociation of disulfides. The results were not convincing since the analytical methods used to detect the expected small amounts of free radicals were too inaccurate.

More recently Schmidt and coworkers⁴ succeeded in isolating several arylsulfur radicals by photolysis of aromatic disulfides or mercaptans in the gaseous state followed by quenching at 77 K.

Photolysis of diaryl disulfides in solution has shown the interaction of two PhS fragments to form thiophenyl-thio-

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phenol type compounds $\mathrm{PhSC}_{6}\mathrm{H}_{4}\mathrm{SH}.^{5}$ Mercaptans and disulfides are well-established dehydrogenating agents. They inhibit, for instance, radiation-induced reduction of benzophenone by 2-propanol.⁶ The mechanism would imply the existence of a thiyl radical. In the gas phase, an absorption band at wavelengths lower than 310 nm was attributed to the phenylsulfur radical by several authors.^{7,8} All these features indicate the existence of PhS but, in contrast to phenoxy radicals, no observations have so far been reported of such species stable at room temperature.

We have applied the method of flash spectroscopy to further studies of the photochemical dissociations of aromatic sulfides and mercaptans. The absorption spectrum of the phenylsulfur radical may be unequivocally identified by studies of the changes produced in its spectrum by substitution of chlorine and amino groups. The results have been compared with those obtained in flash photolysis of diphenyl disulfide and several sulfoxides. In order to verify the stability of the C-S bond in a ring, the transient spectra of several polycyclic molecules were recorded.

Experimental Section

Experiments were conducted in solutions aerated or thoroughly degassed by successive freezing and evacuation. To prevent oxidation of oxygen sensitive compounds, the solvents used were flushed with pure nitrogen. The purity of substances was checked by their absorption, fluorescence spectra (spectrofluorimeter MPF2A, Perkin-Elmer), or melting point. Furthermore, the absorption spectrum of each solution was taken before and after flashing. When decomposition was too high, a new solution was prepared before each flash. Solutions of various pH were prepared with sulfuric acid, potassium mono or dihydrogen orthophosphate, sodium hydrogen carbonate, and sodium hydroxide. pH values were checked with a potentiometer. The flash photolysis apparatus employed two rare gas filled photolysis lamps in series with a flash duration of 4-5 μsec and a discharge energy of 1000 J in a 20-cm path length cell. The spectra were photometered on a Joyce-Loeble microdensitometer. Optical density calibration was carried out with a density wedge. Kinetics were studied using a quartz-iodine lamp and two photolysis lamps in series with a flash duration of 5 μ sec and a discharge energy of 220 J.

Results and Discussion

I. Aryl Derivatives. A. Transient Spectra. 1. Thiophenols. Flash photolysis of outgassed solutions of thiophenol in various solvents resulted in the appearance of a transient absorption with a short wavelength maximum near 297 nm and a continuous band up to 520 nm (Figure 1a). Increasing the pH from 3 M H₂SO₄ solutions to pH 10 slightly increased the optical density without modifying the shape of the absorption.

p-Chloro- and p-aminothiophenol displayed a spectrum with a more intense long wavelength band (Figure 1b,c). The solvent effect was rather pronounced in the case of the amino compound.

Absorption spectra in aerated solutions were identical but generally less intense than those of outgassed solutions and the intensities of the spectra reached a maximum during or immediately after the flash.

The half-life was about 200 μ sec.

2. Sulfides. Methyl phenyl sulfide showed nearly the same absorption spectrum as thiophenol (Figure 2a). Di-



Figure 1. Transients observed from thiophenol (a), p-chlorothiophenol (b), and p-aminothiophenol (c) in C₆H₁₂(-—) and EtOH (----).



Figure 2. Transients observed from methyl phenyl sulfide (a), diphenyl sulfide (b), and benzyl phenyl sulfide (c) in C_6H_{12} (and EtOH (- - - -).

phenyl and benzyl phenyl sulfides (Figure 2b,c) did not display the maximum at 297 nm due to absorption of the parent compounds. Benzyl phenyl sulfide showed an additional sharp band at 317 nm which disappeared quite rapidly in outgassed solutions (~50 $\mu sec)$ and was absent in aerated solutions. From previous work,⁹ this band can be attributed to the benzyl radical.

3. Diphenyl Disulfide. Diphenyl disulfide displayed a band at 352 nm, insensitive to pH and hardly visible in thiophenol and diphenyl sulfide (Figure 3a).

4. Triphenylsulfonium Chloride. The absorption spectrum was observed from 340 nm and consisted of a broad maximum at 370 nm and a continuous absorption up to 620 nm (Figure 3b). The decay time was shorter than 50 µsec.

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The Journal of Physical Chemistry, Vol. 77, No. 12, 1973

350

Parent molecule	Solvent	k/ε, cm sec ⁻¹	$k, M^{-1} \sec^{-2} (\epsilon = 340)$	$k_{c} = 8RT/$ 3000η
Diphenyl sulfide	C ₆ H ₁₄	8.2×10^{6}	2.8×10^{9}	2×10^{10}
Benzyl phenyl sulfide	C ₆ H ₁₄	1.5×10^{7}	$5.1 imes 10^{9}$	2×10^{10}
	EtOH−H ₂ O (1:1)	4 × 10 ⁶	1.4 × 10 ⁹	5.9×10^{9}
	EtOH	3.4×10^{6}	1.2×10^{9}	$5.4 imes 10^{9}$
	Glycerol	6×10^{5}		
	(95%)	or		
		$3.5 imes 10^{4}$		
Diphenyl sulfoxide	EtOH	$4.5 imes 10^{6}$		
4,4'-Ditolyl sulfoxide	EtOH	3×10^{6}		
Belative optical density		Relative optical density	500 µsec	

Figure 3. Transients observed from diphenyl disulfide (a) in C_6H_{12} (-----) and EtOH-H₂O 1:1 (----) and from triphenylsulfonium chloride (b) in H₂O.

450

500

550

<u> 400</u>



Figure 4. Transients observed from diphenyl sulfoxide (a) in EtOH, 4,4'-ditolyl sulfoxide (b) in C_6H_{12} (----) and EtOH (---), and dibenzyl sulfoxide (c) in EtOH.

5. Sulfoxides. On photolysis, outgassed solutions of diphenyl and 4,4'-ditolyl sulfoxides produced slightly different spectra (Figure 4a,b) while aerated solutions showed a very weak absorption. The common absorption maximum in polar and nonpolar solvents were localized at 312 and 420 nm. Dibenzyl sulfoxide (Figure 4c) exhibited only one band at 317 nm which is assigned to the benzyl radical.

B. Decay Kinetics. We studied the decay of transients at room temperature by following the change in light absorption at their 420-450-nm absorption using the photoelectric flash-photolysis apparatus. The decay curves of intermediates derived upon flashing sulfides and sulfoxides gave excellent second-order plots. Some second-order rate constants are collected in Table I. Both k values in glycerol solution of benzyl phenyl sulfide were calculated assuming a two component decay curve (Figure 5, lower

Figure 5. Decay of transient observed at 450 nm from benzyl phenyl sulfide in 95% glycerol solution.

curve). The initial rate of decay (upper curve) was many times faster than the rate of total decay. If the system is initially populated with a random distribution of radicals, some pairs of radicals will be situated close together and will react rapidly. Hence, the measured initial rate constant will be high and will decrease with time as such pairs are consumed. Ultimately, a steady state will be established in which the rate of reaction is limited by the rate of diffusion of radicals toward one another. In this case, we should be able to estimate the extinction coefficient of the radical assuming a diffusion-limited reaction. This hypothesis gave the molar extinction coefficient at 450 nm as 340 in 95% glycerol solution at room temperature. This value allows us to determine the recombination rate constants k assuming that the extinction coefficient is the same in all solvents. The diffusion-controlled rate constants, k_c , calculated using the Debye formula k_c = $8RT/3000\eta M^{-1} \text{ sec}^{-1}$ are also given for comparison. The difference between the experimental and the diffusioncontrolled rates may be attributed to a small activation energy of recombination.

C. Assignment of the Transient Spectra. The two most probable assignments for the transient spectra in sulfides would be to the phenylsulfur radical C_6H_5S or to a phenylsulfur radical ion. The observed independance of solvent, pH, and ionic strength argues against a radical-ion assignment. The absorption spectrum is attributed to the neutral phenylsulfur radical for the following reasons.

(a) The position of its absorption is similar to the spectra of isoelectronic radicals such as benzyl, phenoxyl, and anilino. The absorption spectra of these radicals consist of two separate systems: a sharp band around 300 nm and another transition near 400 nm of varying intensity and sharpness for the three types of radicals.



Figure 6. Transients absorption spectra: (a) benzothiophene, 2×10^{-5} M in EtOH, (b) dibenzothiophene, 5×10^{-6} M in EtOH.

(b) The absorption is common to the photolysis of different molecules.

(c) The longer wavelength light absorption of the paminophenylsulfur radical is attributed to the stabilization of the radical by an electron-donating group in para position.4

(d) All the sulfides showed a permanent absorption at λ <340 nm after flashing. This absorption which was much stronger in polar media and in concentrated solutions of the parent compounds has been identified with the absorption spectrum of diphenyl disulfide. In the case of thiophenol, however, the permanent absorption was more intense in cyclohexane. It has been estimated that about 10% of the original 5 \times 10⁻⁴ M of mercaptan reacted to form disulfide.

The assignment of the absorption bands to a phenylsulfur radical is in contradiction with that postulated by Gaspari and Granzow¹⁰ who observed a transient spectrum with maximum at \sim 420 nm identified as arising from the $\rm R\dot{S}SR^-$ radical anion upon photolyzing aqueous solutions of thiophenol.

A few more comments are necessary in the case of paminothiophenol. The half-life was about ten times higher in ethanol (~500 μ sec) than in cyclohexane. The permanent absorption was intense in cyclohexane but quite low in ethanol. Furthermore, a reversible decrease in optical density of the parent compound at 295 nm has been related to the simultaneous appearance of strong optical density at 360 nm in ethanol solutions. If the parent compound undergoes only decomposition to the thiyl radical under flash photolysis, this would give 9000 as the maximum value of ϵ at 360 nm.

The assignment of radical spectra in 4,4'-ditolyl and diphenyl sulfoxides will be now considered. These spectra show a common band at 312 and 420 nm and a shape similar to that observed in sulfides. We assume, then, that the absorbing species is isoelectronic to that observed in sulfides. The slight difference observed in radical absorption when irradiating sulfoxides and the oxygen effect as well as the absence of the common absorption spectrum in the case of dibenzyl sulfoxide led us to conclude that the radical species was not the thiophenyl radical but could be attributed to the sulfinyl radical C_6H_5SO . Several results from mass spectrometry¹¹ and classical photolysis¹² of sulfoxides suggested the existence of the sulfinyl radical which was thought to be rather stable by analogy with the isoelectronic nitroxide radical R₂NO.



Figure 7. Transients absorption spectra of (a) thianthrene, 2 imes 10^{-6} M, in EtOH, and (b) thioxanthene, 2×10^{-5} M, in EtOH.

II. S-Containing Polycyclic Molecules. Strong absorptions were recorded in carefully outgassed solutions of thionaphthene, dibenzothiophene, thioxanthene, and thianthrene (Figures 6 and 7). From spectrographic experiments the lifetimes seemed to be the same at both maxima excepting thioxanthene where the lifetime at 355 nm was five-ten times longer. The decay of transients was studied with the photoelectric apparatus and followed a first-order process with the lifetimes indicated in Table II. Thioxanthene, however, showed a second-order decay at 355 nm. Since this band was always observed in conjunction with the long wavelength band, this absorption could be due to a radical species arising from the decomposition of the triplet state or of another state which gives rise to the triplet state.

The nature of the transient was identified as a triplet state by the following spectrographic flash photolysis experiment. With a solution containing both sulfur compound and anthracene, the transient absorption disappeared and the triplet-triplet absorption of anthracene was observed. From the results of Table II, it can be seen that the lifetimes in ethanol solutions decrease with the number of sulfur atoms and the number of rings. In the last column of Table II are listed the triplet lifetimes found by Bonnier and Jardon^{13,14} who studied the phosphorescence of biacetyl or benzil sensitized by various concentrations of S heterocyclic molecules in cyclohexane. There is only a maximum factor of 4 between the two series of values.

TABLE II: λ_{max} and Mean Lifetimes of Transients in Some S Heterocyclic Molecules

			Transients	
	M ⁻¹ (in EtOH)	λ_{max}	τ, μsec	τ, ^a μsec
Thionaphthene	1.4 × 10−5	343, 425	108	232
Dibenzothiophene	5×10^{-6}	296, 384	86	20.3
Thioxanthene	2 × 10−⁵	355, 535	58 (535 nm)	40.4
Thianthrene	5 × 10 ⁻⁶	287, 475	49	172

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The Journal of Physical Chemistry, Vol. 77, No. 12, 1973

1482

Conclusions

Photolysis of sulfides results in a bond scission generally confined to the C-S bond, except in the case of thiophenol where S-H scission is favored probably due to the solvent cage effect.¹⁵ The phenylsulfur radical seems more stable than the benzyl radical. It has been recognized that the sulfur lone pair in thiophenol exhibits a considerable amount of π interaction with the adjacent benzene ring¹⁶ and this interaction should stabilize the thiyl radical. The stability of PhS is increased when electron-donating

groups are substituted in the para position. It is rather insensitive to oxygen while the sulfinyl radical PhSO is more sensitive. Irradiation of S heterocyclic compounds produces triplet states with lower lifetimes than those of their aromatic analogs. This observation agrees with the smaller degree of conjugation and stabilization of the π systems across the heteroatom junction.

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Photo-Induced Decarboxylation of Aliphatic Acids and Esters in Solution. Dependence upon State of Protonation of the Carboxyl Group

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The flash photolysis of oxygen-free aqueous solutions of simple aliphatic acids and esters has been studied. Acetic acid, malonic acid, dimethyl malonate, and diethyl malonate have been examined in detail. In all these cases, the major photolytic process observed was the rupture of the C-COOH or C-COOR bond. The .COOH radical was observed from acetic acid, the .COOH and .CH2COOH radicals from malonic acid, and the $\cdot CH_2COOR^1$ radical from dimethyl and diethyl malonate: RCOOH + $h\nu \rightarrow R \cdot$ + ·COOH; RCOOR¹ + $h\nu \rightarrow R$ · + ·COOR¹. The ·COOR¹ radicals decay very fast, with $\tau < 10 \ \mu sec$ in water, to give R^{-1} and CO_2 . On ionization of these acids the quantum yield for this photolytic process is reduced to zero. For acetic acid the ϕ was found to follow exactly the pKa = 4.76 of the ground-state molecule, and for malonic acid the ϕ follows the first pK_a = 2.83 of the ground-state molecule. While photodecomposition of the dissociated acids occurs in aqueous solution, no transient absorption could be observed. The ϕ for the decomposition of the esters was independent of pH in the examined range 1.5-8.0. The photolysis of diethyl malonate produced strong absorptions with $\lambda_{max} \sim 268$ nm suggested to be the result of a Norrish type II reaction. The intermediates produced from the flash photolysis of the keto acids, pyruvic, ethyl pyruvate, and benzovlformic acids are briefly described. No intermediates were observed from the photolysis of acetamide and malonamide.

Introduction

In the study of the action of uv light on peptides and proteins, the photochemistry of end groups (e.g., the carboxyl group) may play a significant role in the inactivation of enzymes. This is of particular interest since it was recently found² that CH₃COOH and HCOOH in water phosphoresce at 77° K and have a triplet energy level (0,0) of ~ 80 kcal. Furthermore, in a study of the direct optical excitation of aliphatic amino acids and peptides in aqueous solution it was found³ that the major intermediates observed on flash photolysis were formed from a photoinduced decarboxylation reaction

$$\begin{array}{ccc} \text{RCH}_2\text{CONHCH}_2\text{COOH} & \xrightarrow{h\nu} \\ & & \\ \text{RCH}_2\text{CONH\dot{C}H}_2 + \dot{\text{CO}}_2\text{H} & (1) \end{array}$$

Very little work appears to have been done on the photochemistry of simple aliphatic acids and esters and their corresponding salts in solution.⁴ None of the primary processes have been established, the nature of the excited state precursors are not known, and indeed the electronic transitions which these molecules undergo have not been clearly defined. One of the reasons for this lack of information must be due to the fact that the carboxyl group

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