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Publication Date

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Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

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ABSTRACT

The deeply colored solutions that result when a wide variety of aromatic sulfides are dissolved in concentrated H_2SO_4 are shown to contain free radicals having the thianthrene nucleus. These result from the condensing and oxidizing properties of concentrated H_2SO_4 . A simplified system in trifluoroacetic acid has been studied in detail, and the radical has been shown to have an oxidation level lying between the monoxide and dioxide of thianthrene. An interpretation of the spin-resonance spectrum permits a choice of a specific radical structure.

CHEMISTRY AND SPIN-RESONANCE SPECTROSCOPY OF RADICALS FROM THIOAROMATIC COMPOUNDS

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INTRODUCTION

Recently it has been reported by Hirshon, Gardner, and Fraenkel¹ that the sulfuric acid solutions of certain sulfur-containing aromatic compounds show electron spin resonance and contain free radicals in substantial amounts. The substances studied include phenyl and p-tolyl disulfides, the corresponding thiols and diphenylene sulfide (thianthrene). No definite hypothesis was made concerning the nature of the free radicals, although the authors seemed to suggest the formation of a biradical. More recently Wertz and Vivo² have also investigated these compounds from the standpoint of the spin resonance. These authors found that if the solutions of the disulfides and thiols are made and examined in the absence of air, two different radicals may be observed. One of these is quite stable and appears to be identical with that obtained from thianthrene.

The work described here was carried out with the object of identifying the stable free radical and determining the nature of the reaction between aromatic disulfides and sulfuric acid.

* On leave from the University of Padova, Italy. International Cooperation Administration Fellow, 1954-56.

¹ Hirshon, Gardner, and Fraenkel, *J. Am. Chem. Soc.* 75, 4115 (1953).

² J. E. Wertz and J. Vivo, *J. Chem. Phys.* 23, 2193 (1955).

EXPERIMENTAL

Eastman Kodak thianthrene with a melting point of 158°C after recrystallization from acetic acid was used. The same was used for the preparation of the oxygenated derivatives. Thianthrene monosulfoxide was prepared by oxidation of thianthrene in acetic acid³ with dilute HNO_3 . The product, when recrystallized from alcohol, had a melting point of 143°C . The isomeric disulfoxides were prepared according to the method of Fries and Vogt.⁴ The trans isomer melted at 284°C and the cis isomer melted at 249°C . Trifluoroacetic acid and 98% reagent-grade sulfuric acid were used. Optical spectra were observed with a Cary Model-14 spectrophotometer. The electron paramagnetic-resonance spectra were taken at a frequency of 9.25 kMc/s on a recording differentiating spectrometer (similar to one developed by Beringer and Castle⁵), using a transmission cavity and bolometer detection.

RESULTS AND DISCUSSION

The solutions of thianthrene in concentrated H_2SO_4 are characterized by two absorption bands in the near infrared with maxima at 10,500 and 9200 Å, one band in the visible at 5460 Å, and three bands in the uv (Fig. 1).

In the range of concentration between 10^{-3} and 10^{-4} mol/l, Beer's Law is not obeyed in the visible and near-infrared region. A tenfold dilution of the concentration produced only an eightfold decrease in absorption. At concentrations around 5×10^{-5} , Beer's Law is obeyed.

In the range of concentrations in which Beer's Law is not followed, the optical densities at the maxima in the near-infrared and visible regions have the same variation with concentration as the spin-resonance signal. It was therefore recognized that these bands are characteristic of the radical.

Although in solutions of diphenyldisulfide in H_2SO_4 (prepared in air) a new weak band is detectable at 7250 Å, absorption of light in the region of the near-infrared and visible wave length that is characteristic of the radical is present. The amount of radical as determined by paramagnetic resonance was found to be proportional to the optical density at 5460 Å.

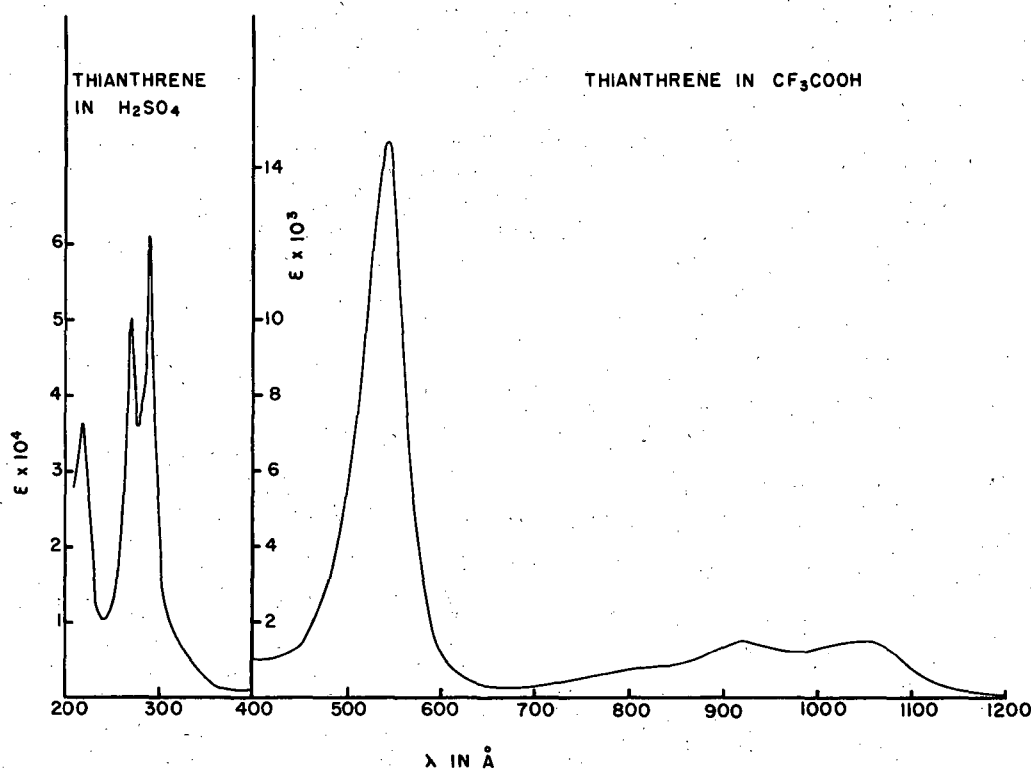
These findings confirmed the observation that the radical obtained from thianthrene and that obtained from diphenyldisulfide in air are identical. All subsequent experiments were, therefore, carried out on thianthrene and its derivatives.

It was interesting to see if thianthrene, after solution in H_2SO_4 , could be recovered as such by diluting the acid. A 2.5×10^{-3} molar solution of thianthrene prepared by shaking three days at room temperature was poured on crushed ice, and the suspension exhaustively extracted with cyclohexane. The uv-spectrum of the cyclohexane layer was compared with the

³ a. K. Fries and W. Vogt, *Ann.* 381, 312 (1911);
b. T. P. Hildritch, *J. Chem. Soc.* 97, 2579 (1910).

⁴ K. Fries and W. Vogt, *Ber.* 44, 756 (1911).

⁵ R. Beringer and J. G. Castle, *Phys. Rev.* 78, 581 (1950).



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Fig. 1. Absorption spectrum of thianthrene radicals in acid solution (10^{-5} M in H_2SO_4 ; 10^{-4} M in $\text{CF}_3\text{CO}_2\text{H}$).

spectrum of thianthrene in the same solvent. The two spectra coincided, but the amount of thianthrene was approximately 50% of the total. The aqueous layer showed a strong absorption band at 2600 Å.

This experiment showed that dissolving in H_2SO_4 transforms some of the thianthrene into a product that is soluble in water (aqueous acid). The product is probably one of the oxides of thianthrene that are known to be slightly soluble in H_2O , possibly mixed with some sulfonation products. That an oxidation is involved is supported by the fact that a small amount of SO_2 is evolved during solution.

After this experiment, it was interesting to see if the radical would be formed by a solution of thianthrene in other acids. Pure trifluoroacetic acid was found capable of dissolving thianthrene and forming the radical. The optical spectrum of the CF_3-COOH solution shows the characteristic bands in the near-infrared and visible regions (uv cannot be observed below 3000 Å) and is much better resolved than in H_2SO_4 (Fig. 1). The band at 10,500 Å is a doublet with maxima at 10,600 and 10,250; an additional weak band was observed at 8000 Å. In the same range of concentrations studied in H_2SO_4 , Beer's Law fails in this system as well.

It appeared from the first quantitative experiments that the amount of the radical formed in trifluoroacetic acid depended on the amount of oxygen available, although even when the solution was made up *in vacuo* and with degassed reactants, a certain amount of the radical (about 5% of the total thianthrene) was always formed. The heating, in a sealed vessel at 80° C, of the solution prepared *in vacuo* causes first a small increase in the concentration of the radical and subsequently a gradual decrease. At equilibrium less than 2% of the initial amount of radical (about 1/100 of the total thianthrene) is left. These experiments suggested that oxygen and oxygenated derivatives of thianthrene play an essential role in the formation of the radical. Since H_2SO_4 is simultaneously an acid and an oxidizing agent, the difficulty of the interpretation of the experiments carried out in H_2SO_4 was recognized. To separate the two effects, subsequent investigations were extended to the oxides of thianthrene *in vacuo*, with trifluoroacetic acid as a solvent.

Six oxides of thianthrene are described in the literature: monosulfoxide, *cis* and *trans* disulfoxides, monosulfone, monosulfoxide monosulfone, and monosulfoxide disulfone. Except for the disulfone, all are known to give colored solutions in sulfuric acid.

We have not been able to prepare, according to the directions of the workers who prepared them originally, the two monosulfones.^{3a} Neither have we been able to find in the literature indications that these compounds have been prepared by others. Rather, it has been found that other investigators⁶ failed in their attempts to prepare them.

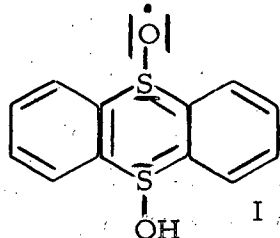
⁶ J. Boeseken and A. T. H. van der Meulen, *Rec. trav. chim.* 55, 929 (1936).

The solutions in trifluoroacetic acid of the monosulfoxide and the two disulfoxides (in the absence of air) are colorless and no radical is present. However, very slowly at room temperature, and more rapidly at 80° C, the usual pink color appears and the solutions show paramagnetic resonance. At 80° C an equilibrium value is obtained in about 15 to 20 hr. The formation of the radical is much faster for the monosulfoxide than for the two disulfoxides. Also, the amount of the monosulfoxide formed at equilibrium is higher. For 1.85×10^{-3} M solutions, 15% of the monosulfoxide and about 3% of either of the disulfoxides is transferred into the free radical.

These results suggest that the free radical is an intermediate state of oxidation between two oxides, possibly mono- and disulfoxide. This hypothesis was tested by measurements of the relative intensities of the spin-resonance absorption obtained at equilibrium from different proportions of mono- and disulfoxide mixed in solution. The results are given in Table I.

These results support the view that mono- and disulfoxide are in equilibrium with each other and with the radical, which is an intermediate state of oxidation between the two.

The hypothesis is made that this radical is of the form



and that it is formed through the following steps:

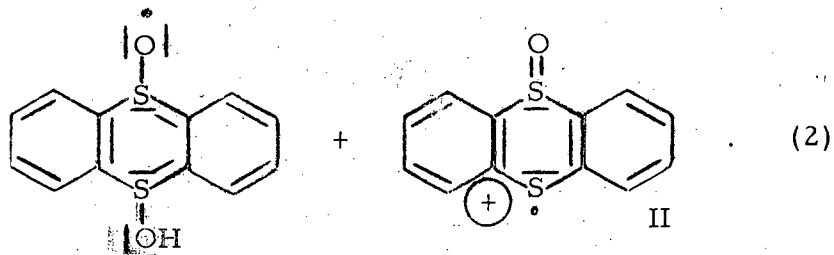
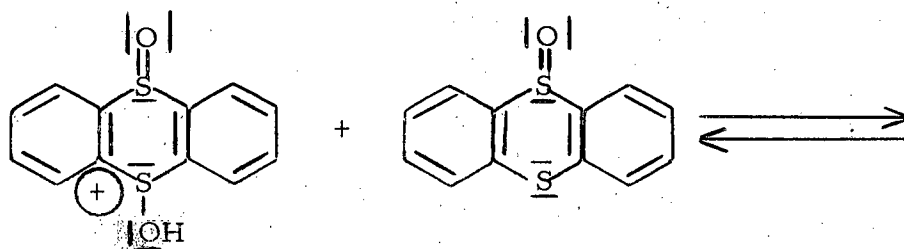
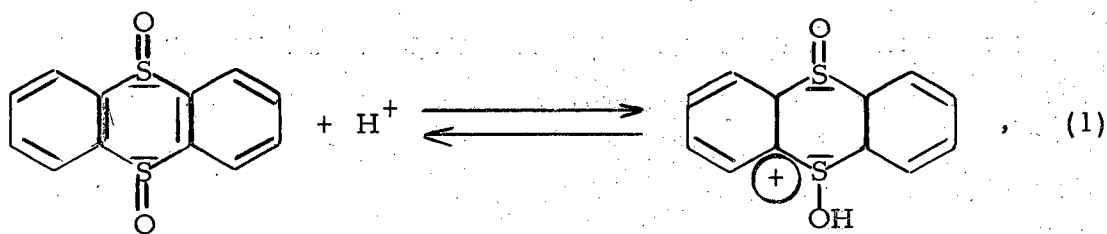
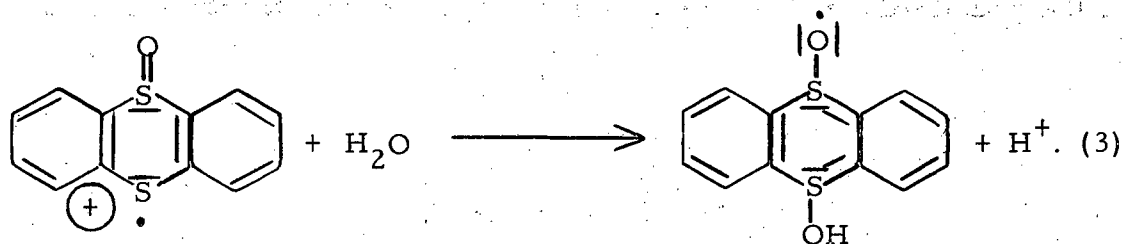


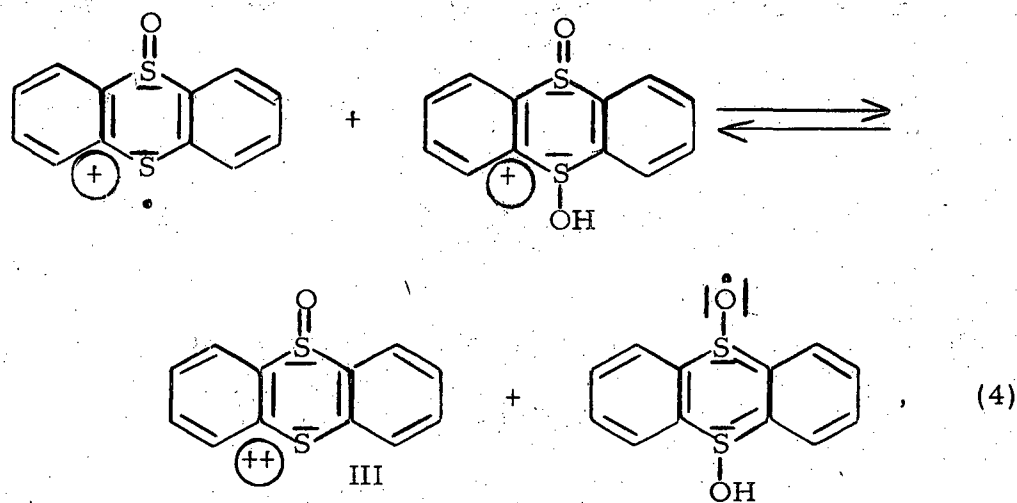
Table I

Concentrations of free radicals (R) in several mixed solutions of thianthrene (T), monosulfoxide (M), and disulfoxide (D)			
Compound(s)	Concentration (mol/l x 10 ³)	Conc. of free radical (mol/l x 10 ³)	Equilibrium Constant $K = \frac{(R.)^2}{(M) \times (D)}$
T	1.85	0.002	-
M	1.85	0.28	-
D	1.85	0.06	-
T } D }	1.85 1.85	0.59	-
M } D }	1.85 1.85	0.80	0.31
M } D }	1.85 3.70	1.33	0.49
M } D }	1.85 7.40	1.75	0.48

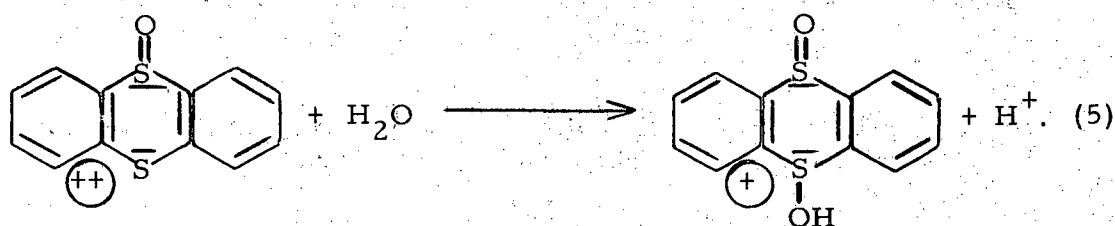
Radical II may now react with a water molecule according to the reaction



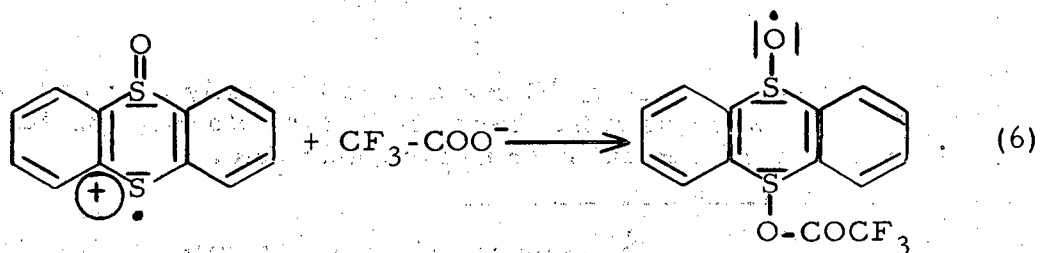
Alternately, II may reduce another disulfoxide molecule according to the reaction



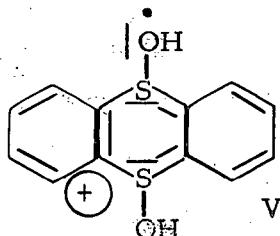
followed by



It has been assumed so far that there is always enough water to perform Reaction 3 (or 5). However, even for an anhydrous acid, similar reactions may be devised. For example:



In sulfuric acid there would be a corresponding derivative. There exists also the possibility that the radical has a symmetric structure such as



or the equivalent with the acyl groups instead of the protons. The relative merit of these structures is discussed later on the basis of the spin-resonance spectrum.

Whatever is the actual structure of the radical, an equilibrium is established:

$$\frac{(R\cdot)^2}{(M) \times (D)} = K \quad (7)$$

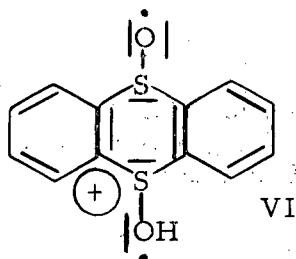
If in the first approximation⁷ it is assumed that we have

$$(M) = (M)_0 - 1/2 (R\cdot), \quad (8)$$

$$(D) = (D)_0 - 1/2 (R\cdot),$$

the equilibrium constant may be calculated. This has been done for those experiments of Table I involving both monosulfoxide and disulfoxide, and the values obtained are shown there.

It may be mentioned that a biradical structure, of the type suggested by Hirshon, Gardner, and Fraenkel¹ for the bianthrone,

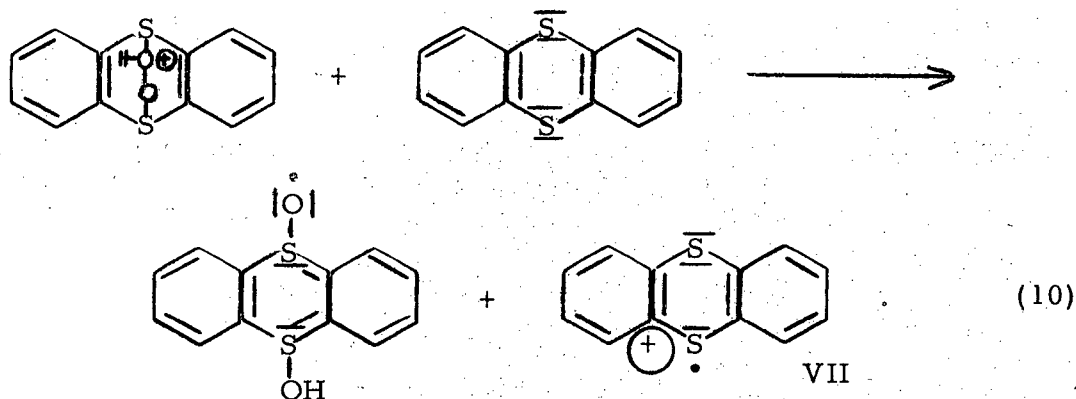
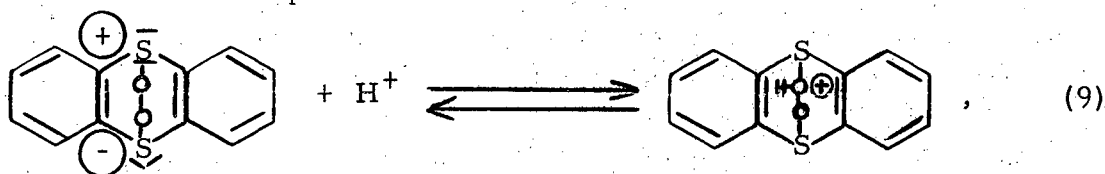


can be ruled out here. In fact, VI could be most easily formed from disulfoxide plus H⁺, whereas it has been shown for both disulfoxides that they hardly form any of the radical in trifluoroacetic acid.

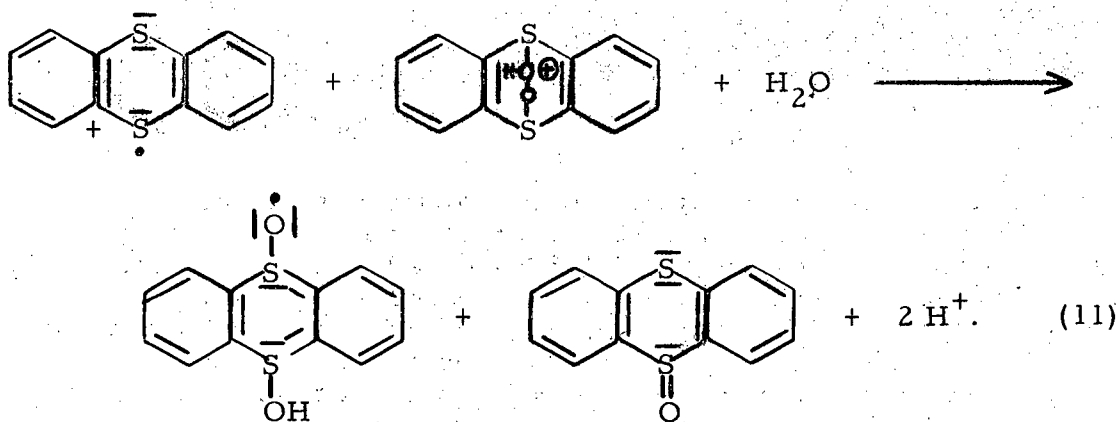
⁷

In this approximation, the amounts of mono- and disulfoxide that might have been transformed through other reactions, disproportionation, and (or) formation of radical dimers, are neglected.

It is of interest to consider that solutions of thianthrene in trifluoroacetic acid exhibit a considerable amount of the radical as soon as they are made up, even when made up in vacuo. It was thought at first that an improper degassing of the reagent was the cause, but repeated careful experiments showed that no matter how the reagents as such are degassed, about 5% of the total thianthrene is immediately transformed into the free radical upon going into solution. We were therefore forced to admit that a certain amount of oxygen is so strongly absorbed into the thianthrene that it cannot be removed by simply decreasing the pressure. Probably, a small fraction of thianthrene is in the form of a transannular peroxide. That the heating of these types of solutions causes the disappearance of most of the radical (exactly the opposite of what happens when the monosulfoxide and disulfoxide are initially present) suggests that here the radical is formed first and subsequently it disproportionates into mono- and disulfoxide until the equilibrium is attained. A tentative explanation for this initial formation of the radical from the transannular peroxide could be



Compound VII could, in the following reaction, reduce another molecule of transannular peroxide, being itself transformed into monosulfoxide by the intervention of a water molecule:



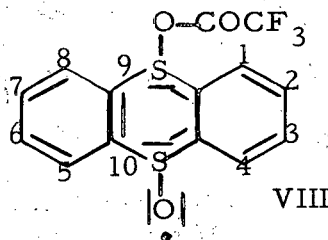
It seems quite reasonable that the above sequence would take place very rapidly, since the transannular peroxide is certainly in a much higher energy state than the isomeric disulfoxide.

The Spin-Resonance Spectrum

As already observed by the previous workers, the free-radical spin-resonance spectrum of this series of compounds consists of five lines with approximate intensity ratios 1:3:5:3:1. A typical derivative curve is presented in Fig. 2. The g value for the center of the pattern was found to be 2.009 ± 0.002 by a comparison with the resonance from crystalline DPPH for which we assumed the g value of 2.0036. The spacing of the five component lines was 1.5 ± 0.1 gauss.

On the assumption that the fine structure is due to the interaction of the magnetic moment of the unpaired electron with nuclear magnetic moments, it is deduced that the free electron interacts with only four protons. Because at least eight ring protons are present in each of the radicals proposed above (I, IV, V), at least nine lines should be expected, if all the protons are equivalent.

However, if the structure of the radical is an asymmetric one, such as Structure IV, in which only the oxygen on Position 10 is bound to an acid residue, it is easily seen, by examination of all the resonance formulae not involving separation of charge, that the free electron may be found on six of the twelve carbon atoms, four of which (2, 4, 5, and 7) are bound to hydrogen atoms. This situation is similar to the nonequivalence of the ring positions observed by Tuttle, Ward, and Weissman⁸ in naphthalene negative ion. If the acid residue is bound to the oxygen on position 9 of Structure VIII, the free electron would interact primarily only with protons on 1, 3, 6, and 8.

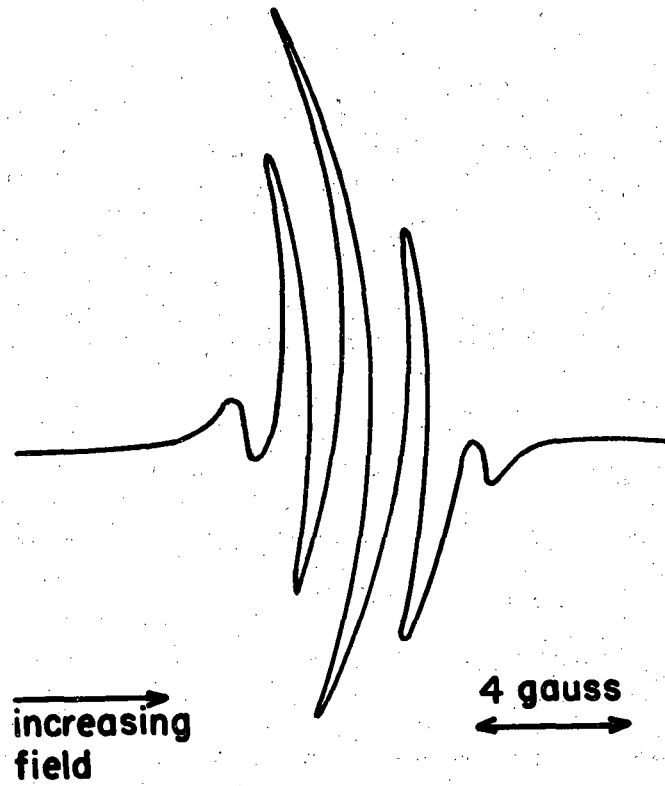


Because IV and VIII are tautomers, the free electron interacts significantly with only four protons at a time.

If this interpretation of the spin-resonance spectra is correct, an asymmetric radical such as IV with no additional protons would be the only one present in large amount.

A search for free radicals of low abundance was made. Three groups of lines with g values sufficiently different from 2.009 were observed. The heights of these lines were about 1/500 of the height obtained for the principal radical above, while the widths were found to be about the same. Two groups consisting of five lines each were found to be symmetrically displaced on either side of the principal resonance by a field of 16 ± 1 gauss. The intensity ratio, hyperfine splitting, and general asymmetric appearance of the individual lines in the two groups are the same as those for the resonance

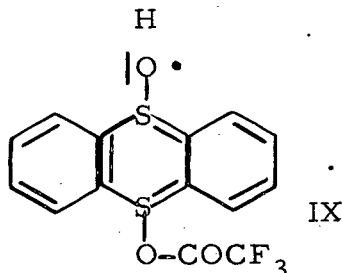
⁸ Tuttle, Ward, and Weissman, J. Chem. Phys. 25, 189 (1956).



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Fig. 2. Typical derivative curve of the spin resonance of the free radical (1.75×10^{-3} mol/liter of radical in $\text{CF}_3\text{CO}_2\text{H}$).

of the principal radical. The intensity of the low-field resonance is about twice that of the high-field resonance. It is suggested that these two groups of lines originate from Radical IX, formed by the addition of a proton to VIII (or IV):



The 32-gauss splitting between the groups is due to hyperfine interaction between the proton on the oxygen and the electron. This may be compared with the 24-gauss splitting that has been attributed to the methyl proton in the radical dimesitylmethyl.⁹ One would expect, because of the greater electronegativity of the oxygen, that the unpaired electron would spend a larger proportion of its time on the oxygen than on the ring positions. In this interpretation, one should expect an equality of intensities for the two groups, which was not observed. However, a g -value difference of 1% for free radicals with otherwise identical spectra seems more unlikely than an explanation such as that above. In this way a g value of $2.009 \pm .002$ falls at the center of the two groups.

The third group of lines has a g value only about 0.025% higher than the principal resonance, with the result that almost all of it is obscured. Three lines are observed on the low-field side and two lines appear on the high-field side of the principal resonance. The splitting is again about 1.5 gauss and the total spread about 15 gauss.

The intensities of these lines are too small to allow their inclusion as part of the main five-line spectra, so we have ascribed them to another free radical with an undetermined number of lines. The superposition of the relatively very intense spectra upon most of this resonance, together with poor signal-to-noise ratio, prevented a detailed study of this radical. However, a division of the 15-gauss spread by the 1.5-gauss splitting suggests the presence of the nine lines that would be expected of a radical of type V with fluoroacetate replacing the hydroxylic groups.

The Reaction between Aromatic Disulfides and Sulfuric Acid

It was interesting to investigate whether aromatic disulfides other than those previously reported by other workers^{1, 2} dissolve in concentrated sulfuric acid with the formation of free radicals. A number of substituted aromatic disulfides have been investigated and the results are given in Table II.

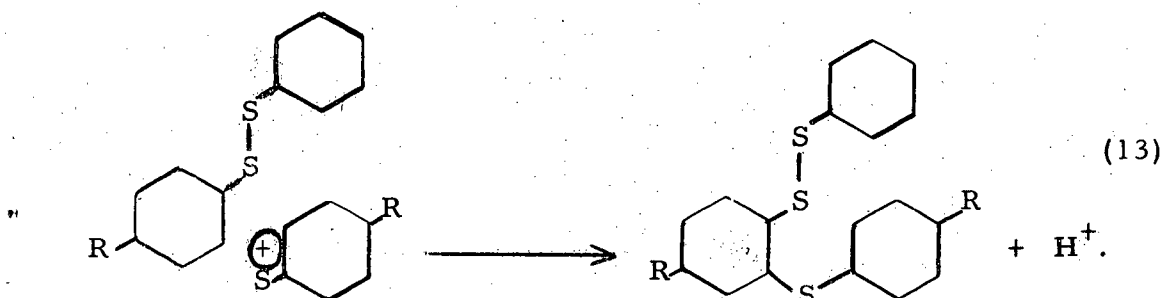
⁹ H. S. Jarrett and G. J. Sloan, J. Chem. Phys. 22, 1783 (1954).

Table II

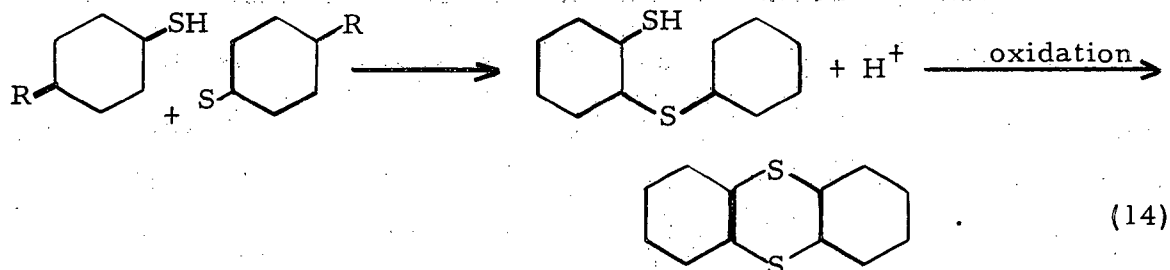
Disulfide	Color of the H_2SO_4 solution	Approx. abundance of free radical
Diphenyldisulfide	purple	5 to 10%
p-tolyl	purple	~ 10%
o-tolyl	blue-green	~ 4%
p-nitro	red	--
o-nitro	yellow	--
p-dimethylamino	colorless	--
o-carboxy	orange-red	1%
p-chloro	does not dissolve	

In analogy with what has been established for diphenyldisulfide, it may be assumed that whenever free radicals are detected a derivative of thianthrene has been formed from the corresponding disulfide. An analysis of the above results shows that, with the exception of the o-carboxy derivative, the disulfides capable of reacting with sulfuric acid to give thianthrenes are those which contain electron-releasing substituents in the ring. When electron-attracting substituents are present, the formation of thianthrenes is prevented.

The following mechanism, consistent with the above observation, is proposed:



This is followed by ring closure and formation of the corresponding thiophenol. The electrophilic attack may occur not only on the disulfide but also on the thiophenol. In this case ring closure occurs with simultaneous oxidation by the sulfuric acid:



In this mechanism it is seen that the formation of thianthrenes is determined by the rate of Reaction (12), (13), or (14). Naturally it is impossible to state which step is the rate-determining one, but whichever it may be, it is easily seen that all reactions are favored by electron-releasing, and hindered by electron-withdrawing, substituents. The only exception to this behavior is offered by the carboxy derivative, and this may be reasonably accounted for by assuming that in sulfuric acid a partial decarboxylation occurs, making possible the subsequent electrophilic attack, Eq. (13).

* * * * *

This work was performed under the auspices of the U. S. Atomic Energy Commission.