Ion Radicals. XII. The Reactions of Diaryl Sulfides and Sulfoxides, Benzene Thiolsulfonate, and Benzenesulfinic Acid in Sulfuric Acid[1,2]

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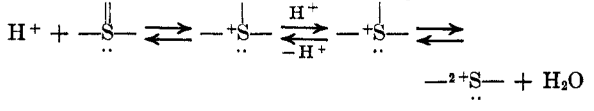
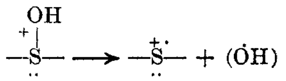
Attempts to prepare the diphenyl sulfide cation radical by the anodic oxidation of diphenyl sulfide (I) and by treating either I or diphenyl sulfoxide (II) with concentrated sulfuric acid were unsuccessful. Solutions of pure I in 96% sulfuric acid were only very slightly colored. These solutions had a very weak, unresolved esr spectrum. Solutions of commercial, unpurified I in 96% sulfuric acid were highly colored and gave the esr spectrum of the thianthrene cation radical. Thianthrene was isolated from commercial I; both thiophenol and diphenyl disulfide also appeared to be present. The intense color occasionally attributed to solutions of I in sulfuric acid seems best attributed to these impurities. Compound I was readily sulfonated on standing in 96% sulfuric acid; a disulfonic acid was formed. Solutions of II in 96% sulfuric acid were initially colorless and had no esr spectrum. On standing for several days, the solutions became pink and had a weak, unresolved esr spectrum with a g value of 2.008. Characterizing this as the spectrum of the diphenyl sulfide cation radical does not seem justified. 4,4′-Dinitrodiphenyl sulfide (III) and sulfoxide (IV) did not give a cation radical in 96% sulfuric acid. Each was recoverable from solution. A solution of IV in 100% sulfuric acid became red with time and developed a weak, single-line esr spectrum. A solution of 4,4′-dihydroxydiphenyl sulfide (V) in 96% sulfuric acid had a five-line esr spectrum; and a solution of 4,4′-dimethoxydiphenyl sulfide (VI) had a nine-line spectrum. This spectrum was also obtained by the anodic oxidation of VI in nitromethane. A solution of di-*p*-tolyl sulfide (VII) in 96% sulfuric acid was initially green and gave a 15-line esr spectrum, each line being further split. The g value was 2.00737. The spectrum, consisting of a heptet (4.9-gauss splitting) split by two quintets (2.7- and 0.6-gauss splitting), is attributed to the *p*-tolyl sulfide cation radical. The same spectrum was obtained from di-*p*-tolyl sulfoxide (VIII) in 96% sulfuric acid. In 95% D_2SO_4, VII gave a seven-line spectrum with splitting 4.9 gauss. An old solution of VII in 96% sulfuric acid was red and gave an esr spectrum of seven lines with a g value of 2.00786 and splitting 1.6 gauss. A disulfonic acid of VII was recovered from such a solution. Solutions of phenyl benzenethiolsulfonate (X) and benzenesulfinic acid (XI) in 96% sulfuric acid were initially colorless but soon went through a series of color changes. Associated with these changes was the development of an esr spectrum. In each case two species were responsible for the esr spectrum. The thianthrene cation radical was formed, albeit in only small amounts. Also, a material was formed which was insoluble in water and organic solvents, but whose 96% sulfuric acid solution had a two-signal esr spectrum. One of the signals with g = 2.0082 resembled that of the thianthrene cation radical; the other had g = 2.0153. For want of a better name this material is called a polymer. Diphenyl disulfide is an early-formed product from the reactions of X in sulfuric acid, while X is an early-formed product from the reactions of XI. Suggestions are made for the reactions that lead to these products and the thianthrene cation radical. Similar results are reported for the reaction of diphenyl disulfide in 96% sulfuric acid.

In previous papers we have described the reactions of thianthrene, phenothiazine, phenoxathiin, and their 5-oxides in acid solutions. These aromatic, heterocyclic sulfides can undergo in concentrated sulfuric acid solutions both a one-electron oxidation to a cation radical and a two-electron oxidation to a dication. The reactions which occur when the 5-oxides are dissolved in sulfuric acid depend to a large extent on the concentration of the acid. In acid solutions of appropriate concentration the 5-oxide may be converted to the deoxygenated cation radical, while in higher acidities deoxygenation to the dication may occur. Proposals for the mechanisms of these several reactions have been made in our papers, and are summarized by eq 1–3.

$$-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}- \xrightarrow{-\bar{e}} -\overset{+\cdot}{\underset{\cdot\cdot}{S}}- \xrightarrow{-\bar{e}} -{}^{2+}\underset{\cdot\cdot}{S}- \qquad (1)$$



$$H^+ + -\underset{\cdot\cdot}{\overset{\overset{\displaystyle O}{\|}}{S}}- \rightleftarrows -{}^{+}\underset{\cdot\cdot}{\overset{\overset{\displaystyle OH}{|}}{S}}- \underset{-H^+}{\overset{H^+}{\rightleftarrows}} -{}^{+}\underset{\cdot\cdot}{\overset{\overset{\displaystyle {}^{+}OH_2}{|}}{S}}- \rightleftarrows -{}^{2+}\underset{\cdot\cdot}{S}- + H_2O \qquad (2)$$



$$-\underset{\cdot\cdot}{\overset{\overset{\displaystyle OH}{+|}}{S}}- \longrightarrow -\overset{+\cdot}{\underset{\cdot\cdot}{S}}- + (\dot{O}H) \qquad (3)$$

Work in this and other laboratories[6,7] has shown that certain diaryl sulfides and sulfoxides are also converted to cation radicals in sulfuric acid solutions, for which conversions proposals such as those in eq 1 and 3 have been made.[6,7] In this communication we clarify the position of diphenyl sulfide in this scheme of reactions, and give our results with some 4,4′-disubstituted diphenyl sulfides.

Paramagnetic species are not detectable in a newly made solution of phenyl benzenethiolsulfonate (X) in 96% sulfuric acid. On standing, however, the solution gives rise to an esr spectrum. The source of the spectrum and the reactions of X in 96% sulfuric acid have now been investigated. Because of the connections of the chemistry of X with that of benzenesulfinic acid (XI) and diphenyl disulfide (XII),[8] and the possible involvement of XI and XII as intermediates in the decomposition of X in acid solutions, we have investigated the behavior of XI and XII in 96% sulfuric acid.

Results and Discussion

Diphenyl Sulfide (I).—Compound I has been described as dissolving in cold, 100% sulfuric acid to give immediately a cherry-red solution. This situation[9] was contrasted to the colorlessness of a similar solution of diphenyl ether and was attributed to the formation of the resonance-stabilized, protonated diphenyl sulfide

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[1] Part XI: H. J. Shine and L. Hughes, *J. Org. Chem.*, **31**, 3142 (1966).

[2] Supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grants No. AF-AFOSR-23-63 and AF-AFOSR-975-66, and the Robert A. Welch Foundation, Grant No. D-028.

[3] Postdoctoral fellow, 1965–1966.

[4] Postdoctoral fellow, 1962–1963.

[5] Postdoctoral fellow, 1963–1965.

[6] U. Schmidt, *Angew. Chem.*, **76**, 629 (1964).

[7] U. Schmidt, K. Kabitzke, and K. Markau, *ibid.*, **72**, 708 (1960).

[8] As illustrated in the elegant work of Kice: J. L. Kice and E. H. Morkved, *J. Am. Chem. Soc.*, **86**, 2270 (1964), and earlier papers.

[9] H. H. Szmant and G. A. Brost, *ibid.*, **73**, 4175 (1951).

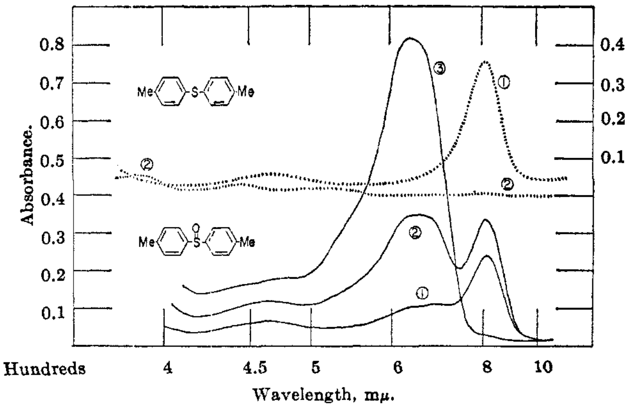


Figure 1.—The visible spectrum of a 4.67 × 10^{-3} M solution of di-p-tolyl sulfide (VII) and di-p-tolyl sulfoxide (VIII) in 96% sulfuric acid. The traces 1 and 2 for VII were obtained 2 min and 18 hr, respectively, after making the solution. The traces 1, 2, and 3 for VIII were obtained 1, 4, and 15 min, respectively, after making the solution.

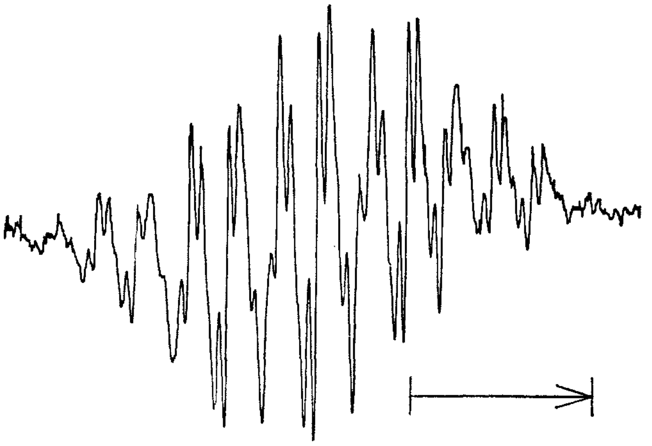


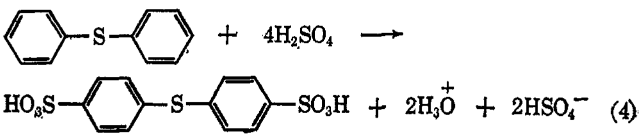
Figure 2.—The esr spectrum of a 0.138 M solution of VIII in 96% sulfuric acid. The solution was 12 min old. The arrow represents 10 gauss and increasing field.

cation. Further interpretation, beyond this point, of the behavior of diphenyl sulfide in 100% sulfuric acid was not given. A high i factor (5.3) was obtained,[9] which is, of course, inconsistent with simply the formation of a stable, protonated diphenyl sulfide cation (for which formation the i factor would be 2.0). It was thought[9] that oxidation reactions and possibly sulfonation reactions produced the high i factor for sulfuric acid solutions of this and other sulfides.

Solutions of diphenyl sulfide in concentrated sulfuric acid have been described elsewhere as being initially colorless, but as becoming colored on standing.[10] The appearance of the color was attributed to oxidation by either air and/or the sulfuric acid.

We have found that solutions of unpurified, commercially-available diphenyl sulfide in concentrated sulfuric acid (96, 98.5, and 100%) are highly colored. The solutions had the absorption and esr spectra of the thianthrene cation radical. We have isolated thianthrene from the commercial product in 0.68% yield. It also appeared, from the behavior of the commercial product during purification, that thiophenol and diphenyl disulfide were present in it. After purification by reduction (to cleave disulfide bonds), washing with sodium hydroxide, fractional distillation, and preparative-scale glpc, the diphenyl sulfide was a sweet-smelling liquid whose sulfuric acid solutions had only a very faint color. It was not possible to obtain a sample of diphenyl sulfide whose sulfuric acid solution was entirely colorless. A 96% sulfuric acid solution of the product obtained after glpc purification had only one weak absorption in the visible, at 544 mμ (the λ_{max} of thianthrene solutions) with ϵ 0.25, compared with the value of ϵ 77 for the unpurified material.

Diphenyl sulfide is readily sulfonated by 96% sulfuric acid. Bourgeois and Peterman[11] reported the formation of the 4,4′-disulfonic acid at 15°. We have confirmed that disulfonation occurs (at room temperature), in at least 78% yield, with no special attempt to optimize the isolation of the acid (as its disodium salt). The formation of a disulfonic acid, if it occurred, in 100% sulfuric acid would be consistent with an i factor of 5.0 (eq 4). This may account for the finding of the value of 5.3.[9]



(4)

It appears to us, therefore, that the reported red color of the solutions of diphenyl sulfide in 100% sulfuric acid is more likely to have been due to impurities in the diphenyl sulfide than to protonated diphenyl sulfide cations; and that, in that strong sulfonating medium, the diphenyl sulfide was probably rapidly converted into the disulfonic acid.

As for the formation of the diphenyl sulfide cation radical from both diphenyl sulfide and diphenyl sulfoxide, along the lines of eq 1 and 3, our evidence gives no real suggestion of success. Solutions of glpc-purified diphenyl sulfide in 96% sulfuric acid gave a very weak esr signal, with none of the hyperfine structure that might be expected from coupling with ring protons. Solutions of diphenyl sulfoxide in 96% sulfuric acid gave a weak esr signal, also without hyperfine structure, only on standing for 1 day or more. It is dubious as to whether either this signal or the one from diphenyl sulfide solution should be attributed to the diphenyl sulfide cation radical.

The formation of the diphenyl sulfide dication in sulfuric acid solution has also been discounted.[12,13] The summary of the situation with diphenyl sulfide and sulfoxide, therefore, is that they do not appear to undergo the reactions depicted in eq 1–3.

4,4′-Dinitrodiphenyl Sulfide (III) and Sulfoxide (IV).—Dilute solutions of III in 96% sulfuric acid were orange, while dilute solutions of IV were colorless. Neither solution gave an esr signal. A solution of IV in 96% sulfuric acid had an ultraviolet spectrum very much like that of IV in ethanol. Each solution had a λ_{max} of 269 mμ, with ϵ^{EtOH} 1.85 × 10^4 and $\epsilon^{H_2SO_4}$ 2.34 × 10^4. Both III and IV were recovered in 96% yield after being kept in 96% sulfuric acid for 3 days. A solution of IV in 100% sulfuric acid became red with age, as has been observed by others;[12] the solution

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[10] W. Dilthey, L. Neuhaus, E. Reis, and W. Schommer, *J. Prakt. Chem.*, [2] **124**, 81 (1930).

[11] E. Bourgeois and K. Peterman, *Rec. Trav. Chim.*, **22**, 349, 356 (1903).

[12] R. J. Gillespie and R. C. Passerini, *J. Chem. Soc.*, 3850 (1956).

[13] S. Oae, T. Kitao, and Y. Kitaoka, *Bull. Chem. Soc., Japan*, **38**, 543 (1965).

had a very weak, broad esr spectrum, whose origin is not known.

4,4′-Dihydroxydiphenyl Sulfide (V) and 4,4′-Dimethoxydiphenyl Sulfide (VI).—The esr spectra of sulfuric acid solutions of V and VI have been reported by Schmidt.[7] We have obtained similar spectra: a five-line one from V and a nine-line one from VI. The nine-line spectrum was also obtained by the anodic oxidation of VI in nitromethane solution. These spectra are most simply attributed to spin coupling with four and eight equivalent ring protons, respectively. The solutions in sulfuric acid were not stable, and, based on our experience with I and di-*p*-tolyl sulfide (VII, see below), there should be little doubt that sulfonation occurred.

Di-*p*-tolyl Sulfide (VII) and Sulfoxide (VIII).—The reactions of these compounds in 96% sulfuric acid are complex. On first contact with the acid both VII and VIII gave a green solution, and each solution had an esr spectrum with 15 major lines.

The visible spectra of these solutions were initially similar (see the two first traces in Figure 1), but the changes which took place in the two spectra were quite different. A feature which was common to the spectrum of each solution was the initial formation and disappearance of a peak at 825 and a band at 460 mμ. We associate this feature with another common one, the formation and gradual collapse of the esr spectrum with 15 major lines (Figure 2). We attribute this esr spectrum to the *p*-tolyl sulfide cation radical (IXe) and believe that this radical is responsible for the 825-mμ peak and 460-mμ band of the absorption spectra. The changes in other regions of the absorption spectra of solutions of VII and VIII were too complex to enable our suggesting further assignments. That is, a dilute solution of VII gradually became colorless and later turned red. The red solution gave a seven-line esr spectrum to which we refer below. A solution of VIII became deep blue on standing. The aged solution did not give the seven-line esr spectrum which was obtained with VII, but gave a single-line esr spectrum whose origin is unknown.

The 15-line esr spectrum of a solution of VIII in 96% sulfuric acid is given in Figure 2. The spectrum was analyzed as consisting of a heptet, with splitting of 4.9 gauss, due to the two methyl groups of IXe, and two quintets, with splittings of 2.7 gauss and 0.61 gauss, due to two sets of four equivalent protons in IXe. The 2.7-gauss splitting was obtained from an overmodulated spectrum (Figure 3), while the 4.9- and 0.61-gauss splittings were obtained from Figure 2. The 4.9-gauss splitting was also obtained from the spectrum of a solution of VII in 95% D_2SO_4 (Figure 4). We believe that in this acid VII became deuterated rapidly before being oxidized to the cation radical. The situation is similar to that obtained with 9,10-dimethylanthracene in D_2SO_4,[14] although in the present case the narrow hyperfine splitting due to deuterium was not resolved. Our attributing the esr spectrum in Figure 2 to IXe is supported by the similarity that this spectrum has to the spectra of the anion radicals of di-*p*-tolyl sulfone[15] and bi-*p*-tolyl.[16] Distribution of the unpaired electron density throughout the sulfone and sulfide radicals *via* p,d-orbital conjugation should make their spectra qualitatively similar and also similar to that of the bi-*p*-tolyl anion radical.

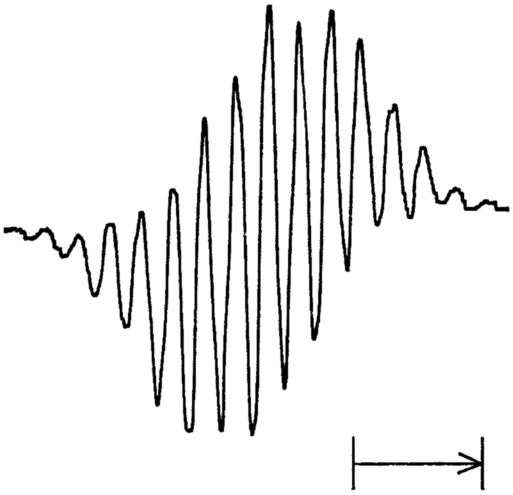

Figure 3.—The overmodulated esr spectrum of a 0.25 *M* solution of VIII in 96% sulfuric acid. The arrow represents 10 gauss and increasing field.

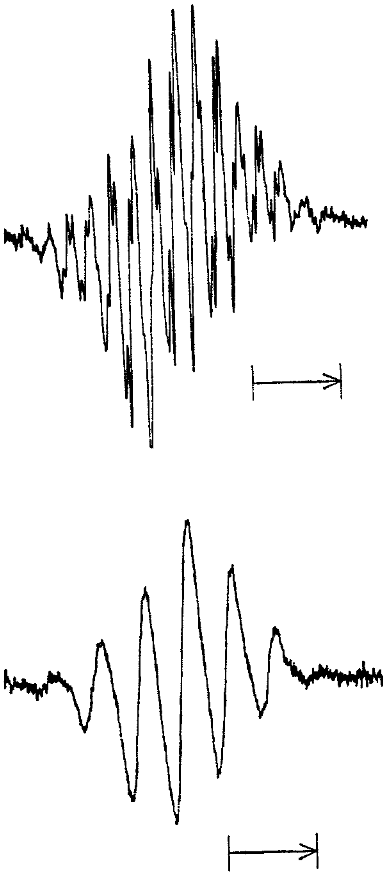

Figure 4.—The esr spectra of VII in 96% sulfuric acid (0.074 *M*, upper) and 95% deuteriosulfuric acid (0.0097 *M*, lower). The arrows represent 10 gauss and increasing field.

Schmidt[7] has given the spectrum of IXe as consisting of seven lines with a splitting of 1.64 gauss and *g* value of 2.0091, assigning the seven lines to splitting by the six methyl protons. This would mean that ring-proton splitting was detectable in the cation radicals IXc and IXd[7] but not in IXe, a contrast which does not seem reasonable. Schmidt's spectrum was obtained with a red solution of VII in sulfuric acid.[6] We have found

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[14] M. C. R. Symons in *Advan. Phys. Org. Chem.*, **1**, 312 (1963).

[15] E. T. Kaiser, M. M. Urberg, and D. H. Eargle, *J. Am. Chem. Soc.*, **88**, 1037 (1966).

[16] K. Ishizu, *Bull. Chem. Soc. Japan*, **36**, 938 (1963).

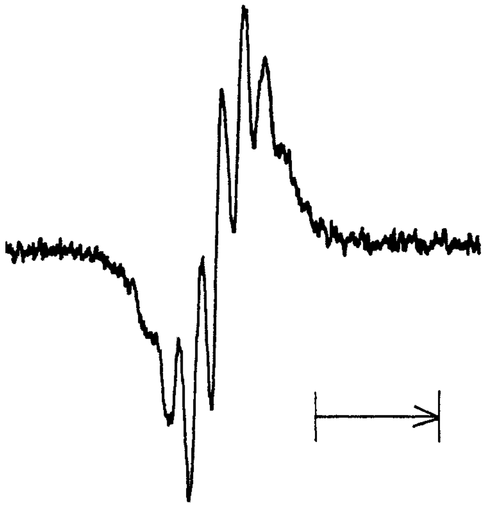


Figure 5.—The esr spectrum of a 0.074 *M* solution of VII in 96% sulfuric acid after 3 days. The arrow represents 10 gauss and increasing field.

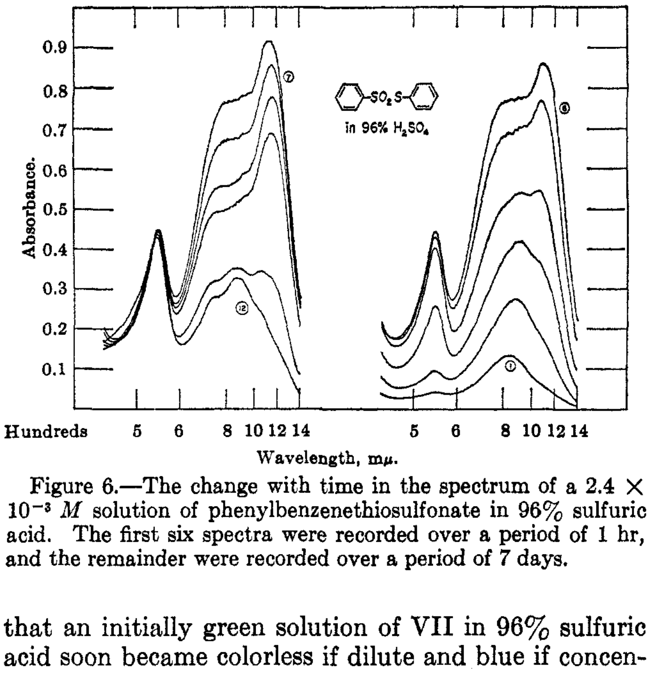
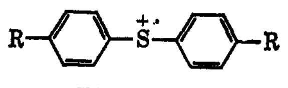


Figure 6.—The change with time in the spectrum of a 2.4 × 10^{-3} *M* solution of phenylbenzenethiosulfonate in 96% sulfuric acid. The first six spectra were recorded over a period of 1 hr, and the remainder were recorded over a period of 7 days.

that an initially green solution of VII in 96% sulfuric acid soon became colorless if dilute and blue if concentrated. In either case the solution later became red. As a dilute, green solution became colorless, the 15-major-line esr spectrum disappeared, and when the colorless solution began turning red a new, seven-line esr spectrum appeared, whose intensity grew with time. With concentrated solutions of VII, the changes in color overlapped, and also the 15-major-line spectrum appeared to collapse with time and re-form as the seven-line one. The seven-line spectrum had a splitting of 1.6 gauss and a *g* value of 2.00786 (Figure 5). This spectrum is probably the same as that reported by Schmidt, although the two *g* values differ. We do not know the origin of the seven-line spectrum. A disulfonic acid was isolated from a red solution of VII in 96% sulfuric acid, but when redissolved in 96% sulfuric acid the disulfonic acid did not give the seven-line esr spectrum. The attempted isolation and identification of other products from the red solution was not successful.

In summary, cation-radical formation was achieved with the diaryl sulfides only when electron-donating substituents were present in the rings, that is to give



IXc, R = OH
d, R = OMe
e, R = Me

IXc–e. Evidently, the presence of these substituents also made the rings susceptible to other reactions, presumably sulfonation, since the radicals were present in low concentration and had a short life.

Phenyl Benzenethiolsulfonate (X).—A solution of X in 96% sulfuric acid was at first colorless but quickly went through a series of color changes from green through violet. The change in the visible spectrum (Figure 6) showed the formation of the 544-mμ peak characteristic of the thianthrene cation radical. The esr spectrum of a violet solution was also like that of the thianthrene cation radical. A sample of X was recovered almost quantitatively after a very short residence in the acid solution. On slightly longer standing (a few minutes only) both X and diphenyl disulfide (XII) were isolated, the amount of the recrystallized XII representing 27 wt % of the unrecovered X. After several hours of standing a solution of X in the acid gave 59 wt % of a solid which was insoluble in organic solvents, and therefore, for want of a better name, will be called a polymer. Along with the polymer was isolated a mixture (10 wt %) of thianthrene and thianthrene 5-oxide.

The absorption spectrum finally achieved by a solution of X was a composite of the thianthrene cation radical spectrum and the spectrum of the so-called polymer. The 544-mμ peak of a 2.4 × 10^{-3} *M* solution of X (Figure 6) was 2.1% as intense as would be expected of a 2.4 × 10^{-3} *M* solution of thianthrene, and so represents the conversion of 1.8 wt % of the X to thianthrene. When a 0.27 *M* solution of X in sulfuric acid was worked up for products, the conversion of X into thianthrene and thianthrene 5-oxide was 9.9 wt %. Thus, the conversion appears to be an intermolecular process.

It is a reasonable assumption that the thianthrene has its origin in the first-formed XII. Formulating a path for the formation of XII from X entails much speculation at this stage. Two possible sequences of reactions come to mind. In the first (eq 5 and 6),

$$\mathrm{ArSO_2SAr + H^+ \longrightarrow ArSO_2H + ArS^+} \quad (5)$$

$$\mathrm{ArS^+ + ArSO_2SAr \longrightarrow ArSSAr + ArSO_2{}^+} \quad (6)$$

benzenesulfinic acid (XI) and the benzenesulfonyl cation are also formed. In the second (eq 7 and 8),

$$\mathrm{ArSO_2SAr + H^+ \longrightarrow ArSO_2{}^+ + ArSH} \quad (7)$$

$$\mathrm{2ArSH \xrightarrow{oxidation} ArSSAr} \quad (8)$$

the benzenesulfonyl cation, but not XI, is formed. The presence of XI in solutions of partly decomposed X could not be detected, a result which may invalidate the sequence of reactions in which XI is a product, but XI itself decomposes rapidly in 96% sulfuric acid, so that, where it may be formed in a sequence of reactions, it may also decompose too fast to build up to a measurable amount. The fate of the benzenesulfonyl cation, if it is formed as in eq 6 and 7, may be its reac-

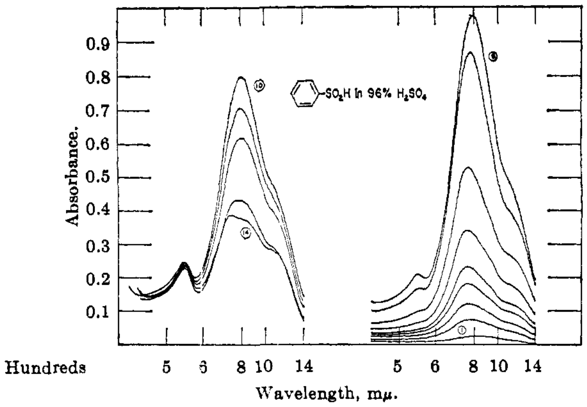


Figure 7.—The change with time in the spectrum of a 1.97 × 10^{-2} M solution of benzenesulfinic acid in 96% sulfuric acid. The first nine spectra were recorded over a period of 2 days, and the remainder were recorded over a further 5 days.

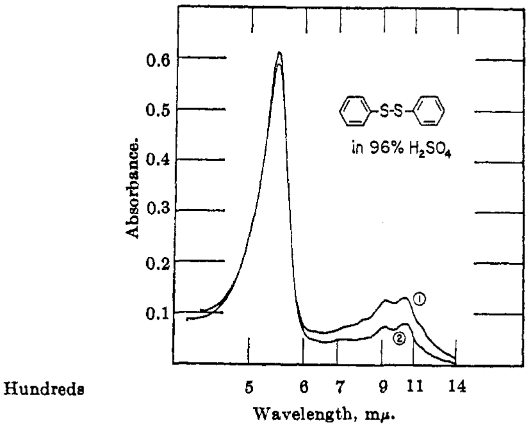


Figure 8.—The spectrum of a 2.08 × 10^{-3} M solution of diphenyl disulfide in 96% sulfuric acid after (1) 4 hr and (2) 12 days.

tion with either water to give benzenesulfonic acid, or other nucleophiles to give polyaryl compounds.

Thianthrene 5-oxide was isolated by Hilditch from the reactions of X with concentrated sulfuric acid.[17] Hilditch's major product was the cream-colored solid which we call a polymer. He described this solid as the monoxide of diphenylene *p*-disulfide, but we feel that this sulfide would have a structure so strained that neither it nor its oxide will exist.

Benzenesulfinic Acid (XI).—A colorless solution of XI in 96% sulfuric acid slowly became greenish blue and later violet. The characteristic 544-mμ peak of the thianthrene cation radical developed in the visible spectrum (Figure 7) and the five-line pattern in the esr spectrum. A 5-min-old solution of XI gave X in 23 wt % yield, which, if the formation of X from XI in the present work follows the accepted stoichiometry,[18] represents almost 40% yield. A 5-hr-old, 2.1 M solution of XI gave a "polymeric" product in 48 wt % yield and a small amount (0.7 wt %) of a mixture of thianthrene and its 5-oxide. The 544-mμ peak of a 1.97 × 10^{-2} M solution of XI in sulfuric acid (Figure 7) was only 0.03% as intense as would be expected of a similarly concentrated thianthrene solution, and so represents only a 0.045 wt % conversion of XI to the thianthrene cation radical. Thus, the two results indicate that the thianthrene was formed by an intermolecular process in the case of XI, as was proposed in that of X. Hilditch[19] obtained 5 wt % of X from XI in concentrated sulfuric acid. The major product was a cream-colored solid, insoluble in all organic solvents, which he described as diphenylene *p*-disulfoxide, and which we call a polymer.

Diphenyl Disulfide (XII).—The color changes and visible spectrum of solutions of XII have been described earlier.[20] The visible spectrum (Figure 8) of a 2.11 × 10^{-3} M solution of XII in 96% sulfuric acid was very much like that of the thianthrene cation radical, but the 544-mμ peak was only 3.3% as intense as would be expected of a 2.11 × 10^{-3} M solution of thianthrene. Solutions of XII which were initially 0.155 M gave very little (2.5–5 wt %) of a water-insoluble product when poured onto ice. The product was a mixture of thianthrene and its 5-oxide. A solution which was initially 0.31 M gave 106 wt % of solid, predominantly of the type we have called polymeric, when poured onto ice containing ferrous sulfate. The purpose of using the ferrous sulfate was to ensure the conversion of the thianthrene cation radical to thianthrene rather than a mixture of thianthrene and its 5-oxide.[21] The amount of thianthrene isolated from the precipitated solid was 8 wt %. Thus, the formation of thianthrene from XII was enhanced by using higher concentrations of XII, which suits an intermolecular reaction, such as proposed by others,[22] rather than an acid-catalyzed, intramolecular cyclization of XII.

The marked effect of changing the concentration of the XII, though, was in what happened to the 90+ % of the XII that did not become thianthrene. What were water-soluble products in the dilute-solution reactions became water-insoluble products in the more concentrated solution reactions. We do not know what these products are. It may be safely concluded, we believe, that the esr spectra of dilute solutions of XII are due to the thianthrene cation radical. Where a solution is sufficiently concentrated to give some of the so-called polymeric product, the esr spectrum will be that of the thianthrene cation radical overlapped by the spectrum of some component of the polymer. It is possible that this component may be a thianthrene unit.

The So-called Polymeric Products.—Each of these, obtained from X, XI, and XII, was a cream-colored solid, insoluble in water and organic solvents. The infrared spectrum of the polymers obtained from X and XII appeared to be identical, and closely like that of the polymer obtained from XI. The three solids were not identical, however, but must have had common structural units. Thus, each solid dissolved in 96% sulfuric acid and gave a blue-violet solution. Each solution had absorbance bands in the regions of 720–730, 870–900, and 1100–1130 mμ, but with different relative intensities (Figure 9). Each solution was paramagnetic. The esr spectrum of the X polymer was a distorted five-line signal with a g value of 2.0082. The esr spectra of the XI and XII polymers contained two groups of lines: a five-line one with a g value of 2.0082 and a weaker, three-line one with a g value of 2.0153.

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[17] T. P. Hilditch, *J. Chem. Soc.*, **99**, 1091 (1911).

[18] J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962).

[19] T. P. Hilditch, *J. Chem. Soc.*, **97**, 2579 (1910).

[20] H. J. Shine and L. Piette, *J. Am. Chem. Soc.*, **84**, 4798 (1962).

[21] This technique was developed in our laboratory by Dr. C. F. Dais.

[22] A. Fava, P. B. Sogo, and M. Calvin, *J. Am. Chem. Soc.*, **79**, 1078 (1957).

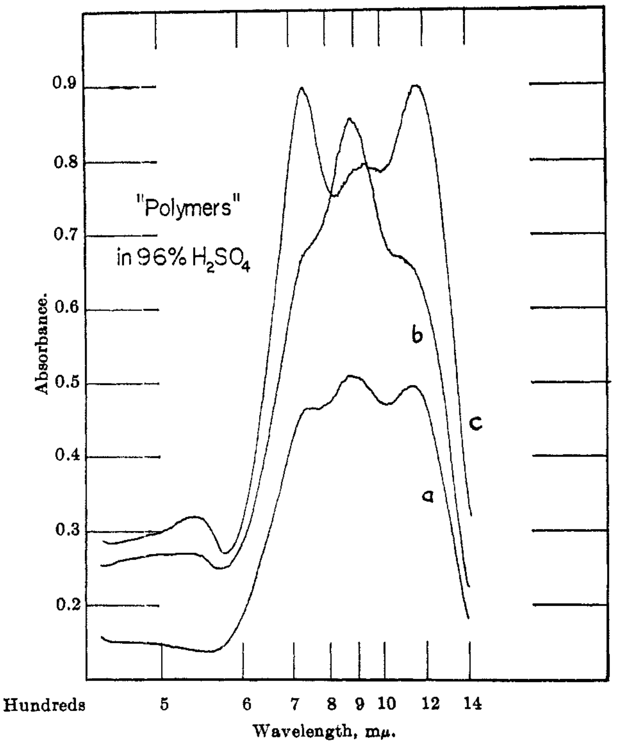

Figure 9.—The spectra of the "polymers" in 96% sulfuric acid: (a) from benzenesulfinic acid, 400 mg/l., (b) from phenyl benzenethiolsulfonate, 400 mg/l., and (c) from diphenyl disulfide, 320 mg/l.

In summary, the esr spectra of solutions of X, XI, and XII in 96% sulfuric acid are attributable in part to the thianthrene cation radical. Much of the X, XI, and XII which is used, however, is converted to products soluble in nothing but sulfuric acid, in which solvent they also give rise to esr spectra.

Experimental Section

Purification of Diphenyl Sulfide (I). A.—The diphenyl sulfide, obtained from Distillation Products Industries, was yellow and smelled of thiophenol. It dissolved rapidly in 98.5% sulfuric acid to give a pink solution which became purple-red on standing. The visible spectrum was closely similar to that of thianthrene in concentrated sulfuric acid. After the solution had been kept for several hours the 544-mμ peak in its spectrum had ε 77. This should be contrasted with the value of ε 8.8 × 10^3 obtained with thianthrene.[20] Two hundred grams of the stock diphenyl sulfide (Ia) was washed with 5% sodium hydroxide solution until the aqueous wash solution was no longer yellow. The sodium hydroxide solution smelled of thiophenol, while the dried (magnesium sulfate) diphenyl sulfide (Ib) had a sweet smell. The Ib was stirred under reflux for 4 hr with granulated zinc and hydrochloric acid, and then washed with 5% sodium hydroxide solution. The yellow wash solution again smelled of thiophenol. The spectrum of the dried diphenyl sulfide (Ic) in 98.5% sulfuric acid was not much changed from that of Ia; ε at the 544-mμ peak was 65. A solution of Ic in dry ether was refluxed with 3 g of lithium aluminum hydride for 1 hr. The suspension was poured onto crushed ice, from which colorless diphenyl sulfide separated. This was washed with 10% sodium hydroxide solution and water, and dried over magnesium sulfate. The dried product was fractionally distilled at 1 mm into nine fractions, the central six of which, comprising 77 g, all distilled between 74 and 74.5° and had, individually, $n^{20}\text{D}$ 1.6319 (lit.[23] $n^{20}\text{D}$ 1.6334). Fraction 7 (Id) gave a very pale pink color in 98.5% sulfuric acid, with $\lambda_{\max}$ 544 mμ (ε 0.5).

B.—Two hundred milliliters (237 g) of Ia was boiled for 15 hr with 200 ml of 4 *N* hydrochloric acid and 20 g of granular zinc. The colorless product was taken up in ether, washed three times with 5% sodium hydroxide solution and water, and then dried over magnesium sulfate. The product was distilled at 1 mm, leaving 16 ml of residue. This crystallized on standing, giving 1.6 g (0.68%) of solid, mp 156–157°. Crystallization from acetone gave a melting point, and mixture melting point with thianthrene, of 158°. The distillate was fractionally distilled five times under reduced pressure, using only the center cuts in each repetition. The fifth distillate (Ie) colored 96% sulfuric acid faintly pink. The visible spectrum had weak, broad bands at 790 and 544 mμ, each with ε approximately 0.25. Glpc showed that Ie contained an impurity, estimated by disk integration to be in about 1.0% concentration. Six preparative-scale chromatograms were run on a 20-ft column of 30% SE-30 on 42–60 Chromosorb P, using an Aerograph Model A-700 instrument with an effluent splitter,[24] to obtain a 1-g sample free of the impurity. The glpc-purified diphenyl sulfide (If) still gave a faint coloration in 96% sulfuric acid solution. The weak 790-mμ band was no longer observed (*cf.* Ie), but a weak band at 544 mμ existed with about the same intensity as seen with Ie.

Diphenyl sulfide (Ia) in 96% sulfuric acid gave rise to the five-line spectrum of the thianthrene cation radical. A weak, broad, unresolved signal was obtained when glpc-purified diphenyl sulfide was used. Attempts to detect an esr signal during the anodic oxidation of diphenyl sulfide (Ie) in nitromethane containing tetrabutylammonium perchlorate were unsuccessful.

Sulfonation of Diphenyl Sulfide.—Twenty milliliters of Ie was dissolved in 50 ml of 96% sulfuric acid by shaking at room temperature for 24 hr. The solution was poured onto ice slurry and brought to pH 5 with sodium hydroxide. The solution was concentrated at 80° and cooled to precipitate a solid of weight 38.5 g when dry. This was recrystallized from aqueous ethanol. Quantitative exchange on a Dowex 50W-X8 column, and titration showed the solid to be the sodium salt of an acid with a neutralization equivalent of approximately 170. An amide was made from the sodium salt and had mp 205–206° (for the 4,4′-disulfonamide of diphenyl sulfide, lit.[11] mp 195°). The bis-S-benzylisothiouronium salt was prepared and had mp 197–199° (aqueous ethanol).

Anal. Calcd for $C_{28}H_{30}S_5N_4O_6$: C, 49.6; H, 4.43; N, 8.25; S, 23.6. Found: C, 50.02; H, 4.79; N, 8.69; S, 23.43.

Diphenyl Sulfoxide (II) in Sulfuric Acid.—The II was obtained from Distillation Products Industries and was recrystallized from a mixture of ether–petroleum ether (bp 30–60°). The melting point was 72–73°. A solution of 1.00 g in 20 ml of 96% sulfuric acid was colorless, but became pale blue-violet after standing for 1 day. The solution had a weak, broad esr spectrum. The 1-day-old solution was poured into water. The solution was extracted three times with ether. The ether solution was washed with sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to leave 975 mg of an oily residue. This was crystallized from ether to give 716 mg of diphenyl sulfoxide, mp 70–72°, in two crops. An oil (180 mg) remained.

A 0.074 *M* solution of diphenyl sulfoxide in 96% sulfuric acid was initially colorless but developed a faint pink color after 1 day. An esr signal could not be detected. After 8 days the pink color had intensified and the solution had a weak, unresolved esr signal, whose *g* value was 2.008 (*cf.* 2.0081 for the thianthrene cation radical).

4,4′-Dinitrodiphenyl Sulfide (III).—Several attempts to prepare this compound by the reaction of *p*-chloronitrobenzene with sodium sulfide[12,25] were unsuccessful. The product was always a yellow solid with a wide melting point range, from which it was not possible to separate a satisfactory sample of III by repeated crystallization. The III was obtained easily by the reaction of *p*-chloronitrobenzene with potassium ethyl xanthate.[26] Crystallization from acetic acid gave pale yellow needles: mp 159.5–160.5°; $\lambda_{\max}$ (95% ethanol) 341 mμ (lit. mp 160–161°,[26] $\lambda_{\max}$ 341 mμ[27]).

Compound III in 96% H_2SO_4.—The solution became orange directly; its spectrum did not change with time. After 14 days it had $\lambda_{\max}$ 265 mμ (ε 2.3 × 10^4), 392 (3.4 × 10^4), and a shoulder at 488 (6.8 × 10^3). A solution of 0.25 g of III in 25 ml of acid was kept for 3 days and poured onto ice. The washed and dried precipitate weighed 0.24 g, and its solution in ethanol had the

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[23] A. I. Vogel and D. M. Cowan, *J. Chem. Soc.*, 16 (1943).

[24] These were performed by Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

[25] R. Nietzki and H. Bothof, *Ber.*, **27**, 3261 (1894).

[26] C. C. Price and G. W. Stacey, *J. Am. Chem. Soc.*, **68**, 498 (1946).

[27] H. H. Szmant and J. J. McIntosh, *ibid.*, **73**, 4356 (1951).

ultraviolet spectrum of III. Solutions of III in 96% sulfuric acid did not give an esr signal.

4,4′-Dinitrodiphenyl Sulfoxide (IV).—The preparation of this compound by the oxidation of III with hydrogen peroxide in acetic acid is given by Szmant and McIntosh.[27] The conditions of the oxidation are not well enough defined for reproducibility, however. Under moderate conditions (equimolar proportions of III and hydrogen peroxide in solution initially at 57° and then at room temperature for 5 hr) much of the III was recovered. With an excess of hydrogen peroxide and a temperature of 70–80° some of IV was obtained, but the major product was the sulfone, mp 252–260°. The best results were obtained as follows. One gram of III in 150 ml of acetic acid was brought to 50°, and 0.5 ml of 30% hydrogen peroxide was added. The solution was kept at 50° for 1 hr and then at room temperature overnight. Dilution to turbidity with water and cooling gave some yellow solid (A). Dilution of the filtrate from A with a large volume of water gave 1 g of colorless solid (B), mp 139–165°. A solution of A in 95% sulfuric acid was bright red while a solution of B was yellow. The ultraviolet spectrum of B in ethanol had λ_{max} 269 $m\mu$ and a small absorption at 341 $m\mu$ (the absorption maximum for III). The product B was crystallized repeatedly from isopropyl alcohol until its ethanol solution showed no absorbance at 341 $m\mu$ and its solution in 98% sulfuric acid was colorless. The product then had mp 178.5–179.5° and λ_{max} (95% ethanol) 269 $m\mu$ (ϵ 1.85 $\times$ 10^4). The loss on repeated crystallization was high, and the yield was 20%.

Compound IV in 96% H_2SO_4.—A 1.57 $\times$ 10^{-2} M solution had a pale tan color. Its absorption spectrum had a small shoulder at 495 $m\mu$ (ϵ 5.8). More dilute solutions appeared to be colorless and had λ_{max} 269 $m\mu$ (ϵ 2.3 $\times$ 10^4). A solution of 43.5 mg in 10 ml of acid was kept for 3 days and poured onto ice. The washed and dried precipitate weighed 41.8 mg and its solution in ethanol had the ultraviolet spectrum of IV. Solutions of IV in 96% sulfuric acid did not give an esr signal.

Compound IV in 100% H_2SO_4.—When first made, a solution of IV in 100% sulfuric acid was pale orange. The color changed with time, becoming redder. A peak developed at 498 $m\mu$; its intensity leveled off at ϵ 48 after 9 days, after which time the solution had a very weak, one-line, broad esr signal.

4,4′-Dihydroxydiphenyl Sulfide (V).—The commercial product (Distillation Products Industries) was Soxhlet extracted with benzene. The benzene-soluble portion was recrystallized twice from benzene to give V, mp 152°.

Compound V in 96% H_2SO_4.—Solutions of V were initially green but quickly became violet. The violet solution had λ_{max} 520 $m\mu$ (ϵ 5 $\times$ 10^2) and 840 $m\mu$ (ϵ 1.4 $\times$ 10^3). After 4.5 hr the solution was again deep green; the broad band at 520 $m\mu$ had almost disappeared while the peak at 840 $m\mu$ had decreased in intensity (ϵ 5.5 $\times$ 10^2). A violet solution gave a five-line, esr spectrum, which became a weak, broad, one-line signal as the solution became green. Attempts to recover identifiable products from solutions of V in 96% sulfuric acid were unsuccessful.

4,4′-Dimethoxydiphenyl Sulfide (VI).—Ten grams of V in 40 ml of 2.5 M sodium hydroxide was boiled with 10 ml of dimethyl sulfate for 2 hr. The cooled solution was extracted with ether. The washed and dried ether solution was evaporated and vacuum distilled at 162° (3.5 mm). The product (4 g) was crystallized from a mixture of ether–petroleum ether to give 3.5 g, mp 42–45°.

Compound VI in 96% H_2SO_4.—Solutions were initially green but quickly became violet. A 2.3 $\times$ 10^{-4} M violet solution had λ_{max} 515 $m\mu$ (ϵ 1.1 $\times$ 10^3) and 870 $m\mu$ (ϵ 3.4 $\times$ 10^3). The violet solution became green on standing, and the solution had λ_{max} 865 $m\mu$ (ϵ 5.4 $\times$ 10^2) with shoulders at 705 $m\mu$ (ϵ 4.3 $\times$ 10^2) and 630 $m\mu$ (ϵ 3.9 $\times$ 10^2). A violet solution gave a broad, nine-line esr spectrum which disappeared as the solution became green.

A violet solution of I g of VI in 20 ml of acid was poured onto ice immediately after the VI had dissolved. An oily precipitate formed. Extraction with benzene gave 725 mg of an oil. Chromatography on alumina with benzene and benzene–ether elution followed by recrystallization of collected fractions gave 175 mg of VI, mp 44–45°, and a small amount of an unidentified solid, mp 78–81°. A similar solution, kept for 3 min before being poured on ice, gave 244 mg of product with similar chromatographic characteristics to those above. When a green, 5-hr old solution was poured onto ice very little precipitation occurred. Attempts to isolate a sulfonic acid were unsuccessful.

Anodic Oxidation of VI.—A 7.7 $\times$ 10^{-3} M solution of VI in spectroscopic grade nitromethane was used. The electrolyte was tetrabutylammonium perchlorate. Nitrogen was bubbled through the solution before the electrolysis. An esr signal was recorded during electrolysis, having nine lines, the central seven of which had relative intensities, 5:16:28:38:30:18:8. The intensities of the two weak end lines could not be measured. The hyperfine splitting was 1.27 gauss.

Di-*p*-tolyl Sulfide (VII).—This was obtained by boiling 2.3 g of di-*p*-tolyl sulfoxide (VIII, see below) in acetic acid (90 ml) and water (10 ml) with granular zinc (10 g) for 21 hr. Extraction of the diluted cool mixture with ether gave 2.2 g of an oil which was crystallized twice from ethanol to give 1.25 g of VII, mp 58.0–58.5°. The use of thin layer chromatography showed the absence of VIII and other contaminants.

Compound VII in 96% H_2SO_4.—Solutions of VII in 96% sulfuric acid were light green when first made. In dilute solutions (4.7 $\times$ 10^{-3} M) this color soon faded; the solution became almost colorless after 45 min and next, after about 18 hr, very slowly became pink. The pink color intensified with time. In concentrated solutions (7.7 $\times$ 10^{-1} M) the initial green color quickly turned bluish violet, and later (after about 6 hr) it became red. The fading and changing of the green color was accompanied by the disappearance of a band at 460 and a peak at 825 $m\mu$. The development of the pink and red colors was accompanied by the appearance of bands at 311, 395, 488, and 520 $m\mu$.

When solutions were either green or greenish blue they gave a 15-line esr spectrum with alternating triplet–quartet hyperfine splittings. The esr spectrum was attributed (with guidance from data obtained with D_2SO_4, below) to a heptet with 4.9-gauss splitting and two quintets, one with 2.7-gauss splitting and the other with 0.61-gauss splitting. The g value was 2.00737. The red solutions gave a seven-line spectrum with a g value of 2.00786. The origin of this spectrum is not known.

Compound VII (2.401 g) was dissolved in 150 ml of 96% sulfuric acid under a helium atmosphere. Helium was passed over the surface of the solution and into a train of tubes containing Ascarite to trap sulfur dioxide. The amount absorbed was 0.1018 g (28% of the theoretical for the total conversion of the VII to the di-*p*-tolyl sulfide cation radical). After 3 days the red solution was poured onto 1500 g of ice slurry. The precipitated solid (A) weighed 94 mg. The aqueous acid solution was extracted twice with chloroform from which 77 mg of B, mp 303–305°, was crystallized, leaving a residue of 178 mg (C). Thin layer chromatography showed C to be a mixture of VII (mainly) and B. The nature of B is not known. The aqueous acid was neutralized with 557 g of barium carbonate. The barium sulfate was removed by filtration and the filtrate was concentrated to give 1.69 g of white solid (D). The neutralization equivalent of the conjugate acid of D, determined after passing a portion through a Dowex 50W-X8 column, was 258. The nmr spectrum of the sodium salt, taken in deuterium oxide, had three singlet peaks at τ 2.22 (2 H), 3.07 (4 H), and 7.82 (6 H). These data indicate that D was the barium salt of a symmetrical di-*p*-tolylsulfide disulfonic acid.

Compound VII in 95% D_2SO_4.—The changes in color and absorption spectra were like those observed with sulfuric acid. The esr spectrum of a 7.5 $\times$ 10^{-2} M solution of VII in D_2SO_4 had seven lines with a splitting of 4.9 gauss.

Di-*p*-tolyl Sulfoxide (VIII).—Commercial VIII (K and K Laboratories) was purified by chromatography on a column of silica gel (Davison, grade 950, 60–200 mesh) using a benzene–ether mixture as eluent. The product was crystallized several times from ether, giving mp 97.5–98°. The use of thin layer chromatography showed no detectable impurities.

Compound VIII in Sulfuric Acid.—Compound VIII dissolved readily in acid solutions. Solutions in 52 and 80% sulfuric acid were colorless and had λ_{max} 240 $m\mu$, the maximum for VIII in ethanol. A solution in 90% sulfuric acid was initially colorless but slowly became blue, with peaks developing at 357, 520, and 820 $m\mu$. A solution in 96% sulfuric acid was wine colored. A peak at 825 $m\mu$ (seen also with VII) disappeared with time while one at 660 $m\mu$ increased in intensity. The esr spectrum of a fresh solution of VIII in 96% sulfuric acid appeared to be identical with that obtained with VII. The g value was 2.00738. As the solution of VIII aged, the 15-line esr spectrum collapsed until, eventually, after 24 hr, a broad, single line was obtained with a g value of 2.00354. The products of reaction of VIII in sulfuric acid were not investigated.

Compound VIII in 95% D_2SO_4.—The absorption and esr spectra were no different from those of VIII in 96% sulfuric acid.

Phenyl Benzenethiolsulfonate (X).—Benzenesulfinyl chloride (78 g) in dry ether was reduced with zinc powder according to

Barnard.[28] The product was a brown oil (37 g). Crystallization of a portion of the oil from ethanol–petroleum ether gave a solid, mp 36–40°. The remainder of the oil was dissolved in benzene and placed on a column of silica gel (Davison, Grade 950, 60–200 mesh). Elution with benzene gave 5 g of diphenyl disulfide, mp 60–61°, and 29 g (49%) of X, mp 45–45.5°. When obtained this way the X was quite easily crystallizable. The recrystallizations of X prior to purification by chromatography were plagued with "oiling-out."

Compound X (1.00 g), obtained as above, was placed on a silica gel column and eluted with four portions of benzene. Each portion was examined by thin layer chromatography, and in none of them was anything but starting material detected. The recovery was 985 mg.

Barnard reports the melting point of his product as 37.5–38.5° and notes that values in the literature are in the range 42–46°.

Phenyl Benzenethiolsulfonate in 96% Sulfuric Acid. Products. A.—Compound X (1.00 g), finely crushed, was placed in a sintered-glass Büchner funnel, which was fitted to a filter flask containing crushed ice. Suction was applied and sulfuric acid was poured into the funnel. The X dissolved rapidly and the colorless, acid solution was sucked continuously onto the ice below. Extraction of the cold, aqueous acid solution with ether, followed by washing, drying, and evaporation of the ether left 948 mg of solid. This was shown by thin layer chromatography to contain only X. Recrystallization from ethanol gave 862 mg, mp 45–46°.

B.—Compound X (4.00 g) was kept in 60 ml of acid for 2 min. The green solution was poured onto crushed ice. Extraction with chloroform, and work-up left 3.47 g of a yellow oil. Column chromatography (benzene–silica gel) gave two solid fractions. The first (1.27 g) gave 653 mg of diphenyl disulfide, mp 56–60°, after recrystallization from ethanol (401 mg, mp 60–61°, after a second crystallization). The second (2.06 g) gave 1.6 g of X, mp 45–45.5°, after recrystallization from ethanol.

C.—A solution of 3.0 g of X in 45 ml of acid was kept for 6 min. Pouring the then-violet solution onto ice gave a small amount of solid which was insoluble in chloroform. Extraction of the aqueous solution with chloroform and chromatography as in B led to 30 mg of diphenyl disulfide, mp 58–60°, and an oil which could not be crystallized.

D.—A 5-hr-old, dark blue solution of 4 g of X in 60 ml of acid gave a solid when poured onto ice. The solid was boiled with ethanol, from which 395 mg of solid was obtained. This was shown by thin layer chromatography to consist of thianthrene and thianthrene 5-oxide. Crystallization from ethanol gave slightly impure thianthrene, mp 154–158°. The ethanol-insoluble solid (2.35 g) was also insoluble in benzene and chloroform. One gram of this solid was boiled with 10 g of zinc and 150 ml of dilute sulfuric acid for 6 hr. The solid appeared to be unchanged. Extraction of the suspension with chloroform gave 15 mg of an oil which solidified on standing. The ultraviolet spectrum (methanol) was that of thianthrene.

E. The Search for Benzenesulfinic Acid.—Two experiments were carried out. In one, 3 g of X in 45 ml of sulfuric acid was poured onto ice after 3 min, and the aqueous acid was extracted with ether. In the other, 2 g of X in 30 ml of acid was poured onto ice after 5 min, but the aqueous acid was not extracted with an organic solvent. The aqueous solutions were titrated with sodium nitrite solution.[18] A precipitate (dibenzenesulfonylhydroxylamine) did not form, and the amounts of sodium nitrite required for the starch–iodide end point were no greater than that for a control on the sulfuric acid alone.

F. The Formation of Benzenesulfonic Acid.—The aqueous acidic solutions from experiments C and D were combined and neutralized with calcium hydroxide. A white solid was obtained after filtering off the calcium sulfate and evaporating the filtrate. Treatment of 0.5 g of this solid with 1 g of S-benzylisothiouronium chloride in water gave 635 mg (70%) of the S-benzylisothiouronium salt of benzenesulfonic acid, mp 142–146°. Crystallization from acetone gave mp 148–149°. A mixture melting point with the authentic salt was the same.

Benzenesulfinic Acid (XI).—This was prepared by the reduction of benzenesulfonyl chloride with sodium sulfite[28] in 63% yield, mp 82–84°.

Benzenesulfinic Acid (XI) in 96% Sulfuric Acid. Products. A.—A colorless solution of 3 g of XI in 30 ml of acid became green-blue very quickly. Pouring onto ice after 5 min and extraction with chloroform gave a yellow oil. Crystallization from ether–petroleum ether gave 700 mg of solid, which on recrystallization from ethanol gave 250 mg of X, mp 43–45°.

B.—A similar solution of XI in acid was kept for 5 hr before pouring onto ice. A solid (1.45 g) precipitated. This was boiled with ether for 2 hr. Evaporation of the ether solution gave 20 mg of solid, which was shown by ultraviolet spectroscopy and thin layer chromatography to be a mixture of thianthrene and thianthrene 5-oxide.

The aqueous acid filtrate was neutralized with barium carbonate. Barium sulfate was filtered off and the filtrate was evaporated to dryness to give 1.45 g of solid. Treatment of 500 mg of this with S-benzylisothiouronium chloride gave the salt of benzenesulfonic acid; after crystallization from acetone 329 mg was obtained, mp 150–151°.

C.—A dark blue, 3-min-old solution of 3 g of XI in 45 ml of acid was poured onto ice. Titration of the solution with sodium nitrite solution showed 0.926 g (30.9%) of XI to be present. A precipitate formed during titration.

Diphenyl Disulfide (XII) in 96% Sulfuric Acid. Products. A.—A violet, 1-day-old solution of 4 g of XII in 120 ml of acid was poured onto ice. A precipitate formed (100 mg), which was found, by thin layer chromatography, to consist of thianthrene and thianthrene 5-oxide.

B.—A dark blue-violet solution, containing 4 g of XII in 60 ml of acid was treated as in A. The precipitate which formed (666 mg) was insoluble in organic solvents. The infrared spectrum of this solid (KBr pellet) was similar to that of the solid obtained in D below, and to those of the organic solvent insoluble solids obtained from X (part D) and XI (part B).

C.—A dark blue-violet, 5-hr-old solution of 2 g of XII in 60 ml of acid was poured onto an ice slurry containing ferrous sulfate. A precipitate (100 mg) formed which was not further investigated.

D.—A dark blue-violet solution of 1 g of XII in 15 ml of acid was treated as in C. A solid precipitated (1.14 g), which, when washed and dried, was boiled with benzene. The benzene solution gave 79 mg of crystals, mp 157–158°, shown by thin layer chromatography to be thianthrene containing a trace of thianthrene 5-oxide. The remainder of the solid was insoluble in the boiling benzene.

Absorption and Esr Spectra.—The visible and near-infrared spectra were recorded with a Beckman Model DK-2 spectrophotometer. Ground-glass-stoppered cells were used. The esr spectra were obtained with a Varian Associates spectrometer, using a dual-sample cavity and potassium nitrosodisulfonate as a standard.

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[28] D. Barnard, *J. Chem. Soc.*, 4673 (1957).