Ion Radicals. VI. Phenoxathiin and Phenoxathiin 5-Oxide in Sulfuric Acid[1-3]

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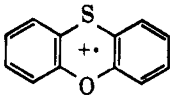
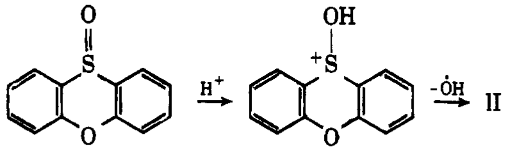
The reactions of phenoxathiin (I) and phenoxathiin 5-oxide (III) in acidic solutions have been studied by ultraviolet, visible, and e.s.r. spectroscopy. It has been shown that in 82, 96, and 100% sulfuric acid III is converted to the phenoxathiin cation radical (II). The conversion of III to II has been followed by changes in the absorption and e.s.r. spectra. A second cation radical (V) is also formed in the 96% sulfuric acid solutions—that of 3-hydroxyphenoxathiin. It is proposed that in acidic solution III is in equilibrium with protonated III (IV) and the phenoxathiin dication (VI); that the formation of the cation radical II occurs by loss of hydroxyl from IV, and that the hydroxyl is stored either as hydrogen peroxide or a peroxysulfuric acid; and that the reactions which eventually lead to V include, first, a hydroxylation of the aromatic ring by attack of water on either of the cations, IV or VI. A hydroxyphenoxathiin 5-oxide (VII) has been isolated from solutions of III in 96% sulfuric acid. The reactions of VII in 96% sulfuric acid have been investigated briefly. The e.s.r. spectrum of a solution of VII in 96% sulfuric acid is attributed to V.

Phenoxathiin (I) dissolves in concentrated sulfuric acid with the evolution of sulfur dioxide and the formation of the ion radical II. The e.s.r. spectrum of II in sulfuric acid has been reported by two groups of workers,[4,5] and an explanation for the 31-line spectrum has been provided by one of them.[4] We have confirmed these observations with I, but our own work, in analogy with the thianthrene and phenothiazine systems reported in previous papers,[2,6] has been concerned more with reactions of phenoxathiin oxide (III). It was shown recently[7] that substituted phenoxathiin oxides are converted by concentrated sulfuric acid into substituted ion radicals corresponding with II, and a general formulation of these transformations was given[7] as shown. In the same work it was noted that the pouring of the radical solutions into water caused the formation of the corresponding phenoxathiin and an aqueous acid solution which contained either hydrogen peroxide or a peracid. This observation is analogous to that made by Fries and Vogt,[8] working with thianthrene oxide solutions.



II



III IV

Drew[9] reported that III, itself, in sulfuric acid solution was converted to the same species as is obtained from I. This species was described by Drew as a thionylium diacid salt, because the pouring of either solutions of I or freshly made solutions of III onto ice gave a mixture of both I and III as products. Drew's observations with I and III are analogous to those we have made in the thianthrene system, for which explanations have been offered.[6] In a further observation Drew noted that, if a solution of III in sulfuric acid was kept for 2 hr. before pouring onto ice, the amount of I recovered was reduced and no III was recovered; instead, a yellow, amorphous product was obtained, which was described as a product of condensation of a molecule of I with one of III. Drew's conclusions are now known to be incorrect.

The purpose of our present report is to account for the reactions of I and III in sulfuric acid.

Results and Discussion

It is already established by other workers that solutions of I in concentrated sulfuric acid contain II. It is also readily predicted from the work of Drew[9] and Schmidt[7] and our earlier work with thianthrene 5-oxide[6] that III will be converted to II in concentrated sulfuric acid. We have followed the behavior of III in acid solutions both by absorption and e.s.r. spectroscopy and present our observations with the help of the figures to follow. In order to make the presentation and discussion of the spectra easier we have listed in Table I the species which we believe were present in the solutions we have investigated and the absorption maxima which we attribute to them. We shall attempt to correlate our proposals for the spectroscopic work with our results from product isolation.

Optical Spectra. A. I in 96% Sulfuric Acid.—Solutions of I in this acid have well-defined ultraviolet and visible spectra (Figures 1 and 2). These solutions obey Beer's law at 244, 276, and 580 mμ over the range of concentrations 1-5 $\times 10^{-5}$ *M*. Other concentrations were not tried. The solutions are also characterized by an e.s.r. spectrum (presented later). We attribute these spectra to the cation radical II.

B. III in 96% Sulfuric Acid.—Solutions of III in 96% sulfuric acid quickly underwent a change in color. The solutions ultimately had spectroscopic characteristics (Figures 1 and 2) very similar to those of solutions of I. If solutions of III in 96% sulfuric acid were kept long enough (an unspecified number of days) they also obeyed Beer's law at peaks at 244, 276, and

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(1) This research formed part of the M.S. Thesis of R. J. Small, Texas Technological College, Aug. 1964.

(2) Part V: H. J. Shine and E. E. Mach, *J. Org. Chem.*, **30**, 2130 (1965).

(3) We thank the Directorate of Chemical Sciences, Air Force Office of Scientific Research, for the generous support of this work under Grant No. AF-AFOSR-23-63. The Beckman recording spectrophotometer used extensively in this work was purchased with funds from the Robert A. Welch Foundation.

(4) B. Lamotte, A. Rassat, and P. Servoz-Gavin, *Compt. rend.*, **255**, 1508 (1962).

(5) M. Tomita, S. Ueda, Y. Nakai, and Y. Deguchi, *Tetrahedron Letters*, **No. 18**, 1189 (1963).

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

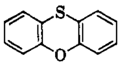
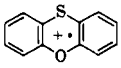
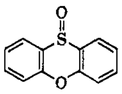
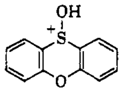
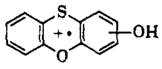
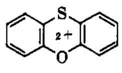
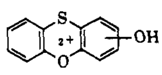
(7) U. Schmidt, K. Kabitze, and K. Markau, *Ber.*, **97**, 498 (1964).

(8) K. Fries and W. Vogt, *Ann.*, **381**, 312 (1911).

(9) H. D. K. Drew, *J. Chem. Soc.*, 511 (1928).

Table I

Allocation of Absorption Maxima to Species in Solution

Species	Symbol	Maxima, mμ		
	I	237	293	
	II	244	276	580
	III	222	298	
	IV	236	316	
	V	277		
	VI	285		512
	VIII	288		

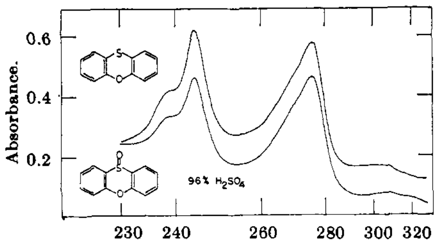


Figure 1.—The ultraviolet spectra of I and III in 96% sulfuric acid. The I solution was 2 days old; the spectrum has been raised 0.1 absorbance unit. The III solution was 7 days old. Both solutions were $2 \times 10^{-5} M$.

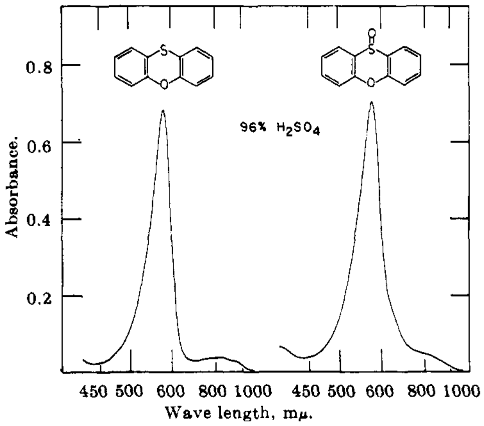


Figure 2.—The visible spectra of I and III in 96% sulfuric acid. The I solution was 2 days old. The III solution was 7 days old. Both solutions were $5 \times 10^{-5} M$.

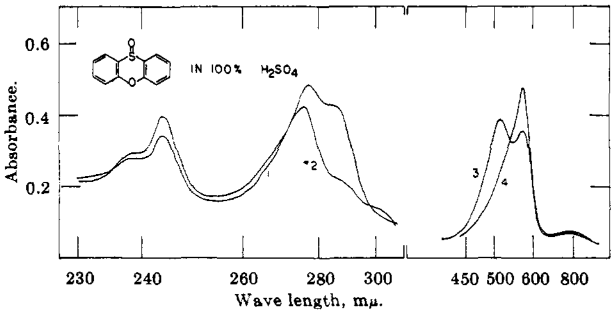


Figure 3.—III in 100% sulfuric acid: ultraviolet spectra of a $2 \times 10^{-5} M$ solution after (1) 2 min. and (2) 10 min.; visible spectra of a $4 \times 10^{-5} M$ solution after (3) 4 min. and (4) 4 hr.

576 mμ. The last wave length is a little lower than that of solutions of I. Although the spectra of I and III in 96% sulfuric acid are very similar there are some differences that need to be noted. The absorbance of the III solution was slightly lower at 244 mμ than at 276 mμ. The absorbances (Figure 1) were 0.448 and 0.465. The reverse was true of the solution of I. Here the absorbances were 0.498 and 0.452. In the visible region, apart from the 4-mμ difference in the major peak, the solution of III showed an absorbance near 650 mμ that was absent from the solution of I.

We assign the peaks at 244, 276, and 576 mμ again to the cation radical II. The differences between the spectra of I and III in 96% sulfuric acid are attributed to the presence of the cation radical V in the solutions of III.

C. III in 100% Sulfuric Acid.—The conversion of III to II in 96% sulfuric acid was more rapid than the analogous reaction of thianthrene oxide[6] so that it could not be followed so easily by absorption spectroscopy. On the other hand, whereas solutions of thianthrene oxide were stable in 100% sulfuric acid,[6] those of III underwent a change with time that could be followed nicely. This change is seen in the ultraviolet and visible regions (Figure 3).

Our assignments here are the 285-mμ band and 512-mμ peak to the dication VI, each disappearing with time as II is formed. The assignments for VI were made with the help of the results from work with III in fuming sulfuric acid and 82% sulfuric acid.

D. III in 30% Fuming Sulfuric Acid.—The visible spectrum of III in 30% fuming sulfuric acid consisted of a single slender peak at 512 mμ which underwent a small decrease over a period of 2 hr. The ultraviolet spectrum of a similar solution consisted initially of a single peak at 285 mμ, and this slowly diminished over a period of several hours. These changes were not associated with an ion-radical formation, such as were the changes seen in Figure 3. We believe that in 30% fuming sulfuric acid III slowly becomes sulfonated or cleaved. We propose that the initial spectra with maxima at 285 and 512 mμ, however, were due to VI and allow us to characterize the dication.

E. III in 82% Sulfuric Acid.—A solution of III in 82% sulfuric acid was initially colorless. In time the solution become purple. The change was followed by e.s.r. and absorption spectroscopy. The growth in the intensity of the color is recorded in Figure 4. The peak that formed was at 576 mμ and is assigned to II.

The ultraviolet spectrum of III in 82% sulfuric acid consisted initially of two large, broad bands at 225 and 236 mμ, and a smaller one at 316 mμ. Each of these disappeared with time (Figure 4) and gave way to the spectrum of II. The band at 225 mμ is comparable with that of III in 95% ethanol (Figure 5). Therefore, we assign this band in Figure 4 to III. We assign the bands at 236 and 316 mμ to IV, the conjugate acid of III, through which we believe the transformation of III to II occurs.

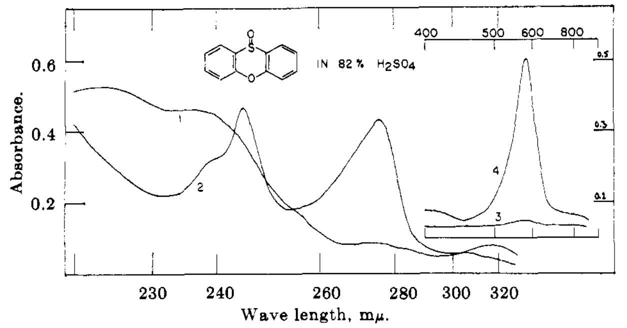


Figure 4.—III in 82% sulfuric acid: ultraviolet spectra of a 2×10^{-5} *M* after (1) 3 min. and (2) 219 min.; visible spectra of a 4×10^{-5} *M* solution after (3) 3 min. and (4) 24 hr.

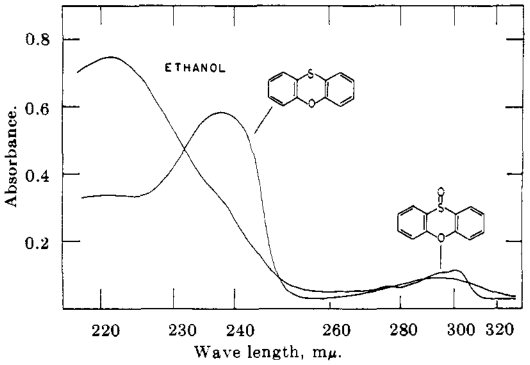


Figure 5.—The ultraviolet spectra of I and III in 95% ethanol. Both solutions were 2×10^{-5} *M*.

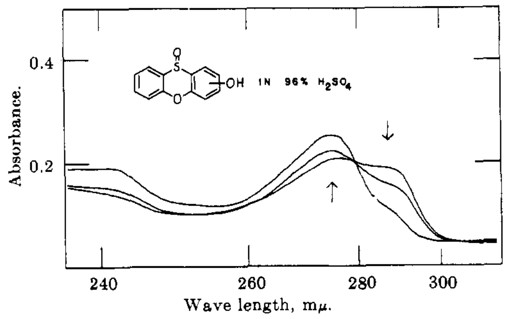


Figure 6.—The change with time in the ultraviolet spectrum of VII in 96% sulfuric acid. The scans were made at 12 min. and 1 and 24 hr. from dissolving.

F. Hydroxyphenoxathiin 5-Oxide (VII) in 96% Sulfuric Acid.—This oxide was isolated from a solution of III in sulfuric acid. The isolation is described in the Experimental section. Solutions of VII in 96% sulfuric acid underwent changes analogous to those of III; they are represented by the ultraviolet spectra in Figure 6. The change from absorbance at 288 mμ to a peak at 277 mμ was accompanied by the formation of a radical, whose e.s.r. spectrum was recorded. We assign the 288-mμ absorption to the hydroxy dication VIII, and the peak at 277 mμ to the hydroxy cation radical V.

E.s.r. Spectra of I, III, and VII in 96% Sulfuric Acid.—These are given in Figure 7. The spectrum C was obtained from I. It is of the cation radical II and appears to be identical with that given for II by Tomita.[5]

The e.s.r. spectrum obtained from VII is given as A. We conclude that this is the spectrum of the cation radical V. It has three major peaks, an apparent anomaly that is also observed in the spectrum of the 2-hydroxythianthrene cation radical.[10,11] Schmidt[7] has shown that substituents in the phenoxathiin rings cause a loss of much of the hyperfine structure of the parent radical II. The indication is that substitution causes a notable change in the coupling constants of the remaining protons.

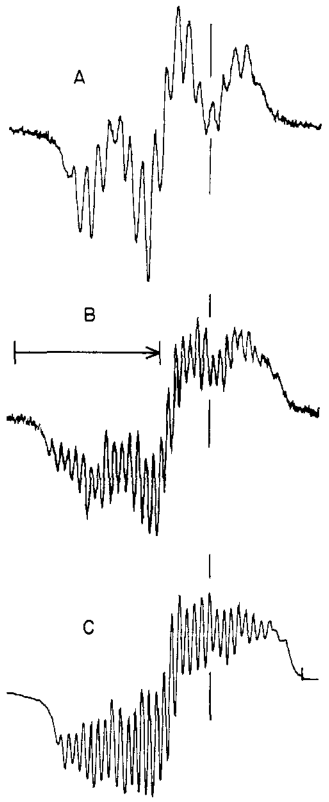


Figure 7.—The e.s.r. spectra of solutions in 96% sulfuric acid: A, VII, 1 hr. old; B, III, 7 days old; C, I, 2 days old. The vertical line indicates the center of a potassium nitrosodisulfonate spectrum. The scale mark is 10 gauss and indicates increasing field.

The *g* values, 2.0059 for II and 2.0062 for V, are in accord with the values given for II and some substituted II radicals by Schmidt.[7] The *g* value of II is smaller and the over-all width of its spectrum (7.9 gauss) is larger than that obtained with the thianthrene cation radical (2.0081 and 5.26 gauss).[11] Therefore, localization of the unpaired electron on the hetero atoms in the thianthrene cation radical appears to be the greater, and spin-orbit coupling with these atoms appears the more pronounced.

A freshly made solution of III in 96% sulfuric acid had an e.s.r. spectrum identical, as far as we could tell, with C. Over a period of time this spectrum both grew in intensity and changed in character. The spectrum of a 7-day-old solution is shown as B. We have concluded from the optical spectra (Figures 1 and 2) that a solution of III in 96% sulfuric acid contains both II and V. The presence of II and V in the same solution would result in an overlap of their e.s.r. spectra. Inspection of Figure 7 shows that this overlap can account for the character of the spectrum B. The imposition of the triplet of spectrum A on spectrum C can be seen in the difference in the relative intensities of the hyperfine lines of B and C.

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[10] H. J. Shine and T. A. Robinson, *J. Org. Chem.*, **28**, 2828 (1963).

[11] H. J. Shine, C. F. Dais, and R. J. Small, *ibid.*, **29**, 21 (1964).

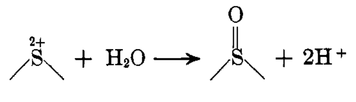
Products.—We have confirmed Drew's observation that the pouring of sulfuric acid solutions of either I or III onto ice gave a mixture of I and III as products. Where I was the solute the recovery of products was uncomplicated. It was found that the amount of III formed could be diminished by including ferrous ion in the system. The results are given in Table II. It can be seen that ferrous ion in the ice slurry causes a drop in the amount of III formed. The effect of ferrous ion on the distribution of products has been studied extensively in the thianthrene and thianthrene 5-oxide system.[12] The ferrous ion in the ice slurry diminishes the formation of the oxide (in the present case, III) when the acid solution is poured onto the slurry. The oxide may originate in these systems from the hydrolysis of the dication (eq. 1) or from the oxidation of phenoxathiin by the hydrogen peroxide formed in the hydrolysis of the ion radical (eq. 2).

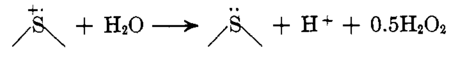
TABLE II

PRODUCTS RECOVERED FROM SOLUTIONS OF PHENOXATHIIN IN 96% SULFURIC ACID

Time in soln., hr.	Use of $FeSO_4$	Products, % I	III	Total
24	. . .	56.5	48.7	105.2
576	. . .	50.2	45.8	96
2	*a*	83.2	. . .	. . .
24	*a*	73.9	15.6	89.5
24	*b*	77.9	16.8	94.7

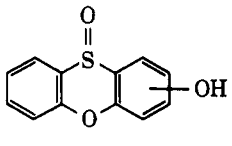
[a] In the acid and in the ice slurry. [b] In the ice slurry only.


(1)


(2)

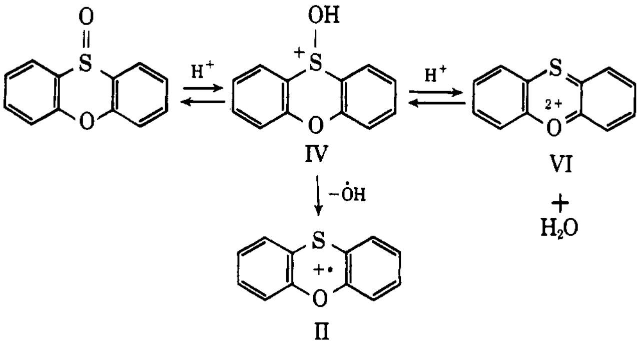
The ferrous ion diminishes, by reduction, the extent of either or both of these reactions. In the present case it appears that it is probably with reaction 2 that the ferrous ion interferes, since there is no evidence for the presence of the dication in the 96% sulfuric acid solutions of I.

The isolation of products from solutions of III was not so simple as from solutions of I. We were able to isolate I and III and to show that the amount of I formed was increased by pouring onto an ice slurry containing ferrous sulfate. Nevertheless, we were unable to achieve satisfactory product separation and balance and therefore cannot tabulate quantitative results as has been done with solutions of I. We have confirmed Drew's observation that the pouring of 2-hr.-old solutions of III onto ice gave a product other than I or III. We have isolated the hydroxyphenoxathiin oxide, VII, from such a system.


VII

Discussion

The formation of the cation radical II from I is an oxidation that is entirely analogous to oxidations in the thianthrene[6] and phenothiazine systems.[2] The behavior of the oxide III is also analogous to that of thianthrene 5-oxide and phenothiazine 5-oxide. Our interpretation of the results with III is as follows. In acid solutions III is in equilibrium with the cations IV and VI, the relative concentrations depending on the initial concentration of III and the strength of the acid.



In fuming sulfuric acid the formation of VI is complete, but the VI is slowly destroyed by other reactions, whose nature is unknown to us. In 96% sulfuric acid two reactions occur. One is the loss of hydroxyl from IV that gives II. The other leads to V. The presence of V in solutions of III in 96% sulfuric acid results not only in the overlapping e.s.r. spectra (Figure 7, B) but also in the additional absorbance at 276 mμ, the position of one of the maxima of II, and hence in the anomalous ratio of absorbances at 276 and 244 mμ, which we have recorded.

The formation of V in solutions of III results from a hydroxylation reaction, whose nature has also been discussed in the case of phenothiazine 5-oxide.[2] It is of interest to note that the hydroxy cation radical does not appear to be present in solutions of III in 100% sulfuric acid (Figure 3), at least, by virtue of the absence of a shoulder in the smooth descent of the long wave-length side of the peak due to II. The absence of V from the 100% sulfuric acid solutions would be in accord with hydroxylation occurring *via* the nucleophilic attack of water on a cation—a reaction that would not occur in 100% sulfuric acid. The hydroxylation may be formulated as either the attack of water on the dication VI or the monocation IV (see Chart I).

The conversion to the cation radical V is viewed as following one of the routes (*i.e.*, *via* oxidation of intermediates IX or X) discussed in the previous paper.[2] We do not know the position of the hydroxy group in the isolated oxide VII. It is represented as being in the 3 position of IX and X from consideration of the most likely charge distribution in IV and VI.

Our proposals for intermediates in the reactions of III in aqueous sulfuric acid include an assignment of ultraviolet bands to the protonated oxide IV. We were unable to make the analogous assignment in the case of phenothiazine 5-oxide.[2] The difference between the two cases may be that the dehydration of the protonated phenothiazine oxide to the stable phenazo-

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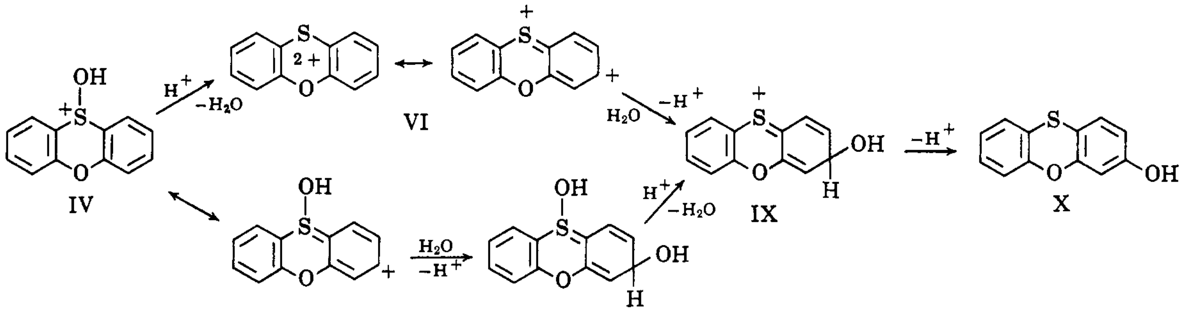
[12] Unpublished work of C. F. Dais.

CHART I



thionium ion may be so easy that it occurs even in aqueous solutions. The analogous reaction with III cannot occur.

Experimental

Materials.—Phenoxathiin (Distillation Products Industries) was crystallized from petroleum ether (b.p. 40–60°) and had m.p. 56.5–57.5°. Phenoxathiin oxide (Matheson Coleman and Bell) was boiled with aqueous 10% sodium hydroxide solution to remove a yellow impurity and was crystallized from ethyl alcohol, m.p. 153–154°. Concentrated sulfuric acid was Baker's analyzed reagent grade, approximately 96%. Where 100% sulfuric acid was used it was made from the former by adding Baker's analyzed 30% fuming sulfuric acid. Duplicate analyses showed the 100% acid to assay as 99.95%.

Product Recovery.—Solutions were made by dissolving 0.01 mole of I or III in 100 ml. of 96% sulfuric acid. Acid containing ferrous sulfate was prepared by stirring the acid with 5 g. of the heptahydrate salt overnight and decanting from the excess of salt before dissolving the I or III. The solution was allowed to stand in the dark for the desired time before pouring onto an ice slurry. Where it was necessary to have ferrous ion in the slurry before pouring the acid the amount of heptahydrate salt used was about 1 g. in about 250 g. of ice.

The solid precipitated by pouring onto ice was washed with water, dried, and weighed. Where I was the solute the precipitate (P1) and filtrate at this stage were almost colorless. Where III was the solute both P1 and filtrate were reddish brown. Precipitates (P1) obtained from solute I consisted of I and III, from which the I was removed with petroleum ether.[9] The separated components were identified as I and III by melting point and ultraviolet spectrum. Separations as clean as this were not achieved when III was the solute. The identification of I and III in the P1 was made by fractional separation and recrystallization using petroleum ether and ethyl alcohol as solvents, but the quantitative analysis of the P1 was not achieved.

The aqueous acid filtrate was neutralized by adding sodium hydroxide pellets while cooling. A second precipitate (P2) was obtained. Where I was the solute, P2 was found to be mainly III. Where III was the solute P2 consisted of III and hydroxy III (VII); we are not certain that other products were not present. Where ferrous sulfate had been used in an experiment, neutralization of the filtrate from P1 caused the precipitation of iron hydroxides as well as P2. In this case the P2 was removed with ethyl alcohol after filtration of the precipitated solids.

In the shaking of ferrous sulfate with concentrated sulfuric acid, the odor of sulfur dioxide was not detected after 24 hr., and the ferrous content of the mixture was no different from that of the ferrous sulfate weighed out.

The Isolation of VII.—Using the procedure above (no ferrous sulfate) the neutralization of the orange-colored filtrate from P1 gave 0.48 g. of gray-colored P2. The P2 was triturated with dilute sodium hydroxide solution leaving 0.16 g. of undissolved III, m.p. 151–154°. The sodium hydroxide solution was treated with carbon dioxide and the white solid obtained was filtered, washed with water, and dried, giving 0.08 g. of product. The same procedure was repeated several times and the combination of the solids precipitated by carbon dioxide was crystallized several times from aqueous ethanol. The final product had m.p. 201.5–202° dec.

Anal. Calcd. for $C_{12}H_8O_3S$ (232.2): C, 62.07; H, 3.47; S, 13.78. Found[13]: C, 61.98; H, 3.67; S, 13.47.

Absorption Spectra.—An appropriate volume of a 1×10^{-4} *M* stock solution of I or II in ethanol was pipeted into a 50-ml. volumetric flask and evaporated to dryness by suction. Acid was then added to the flask. The ultraviolet and visible absorption spectra were recorded with a Beckman Model DK-2 spectrophotometer.

The arrows in the figures indicate either growth or fall at a particular wave length.

E.s.r. Spectra.—The instrument and calibration accessories have been described earlier.[11]

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(13) Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.