

25.00 \pm 0.02°. After the solvent had been equilibrated for at least 30 min., a weighed sample of ester was introduced.

Kinetic runs in acid were done in a sealed ampoule at 125.0 \pm 0.1°.

Absorbance Measurements.—The hydrolysis of ethyl thionbenzoate in base was followed by measuring the absorbance of the reaction mixture at 414 $m\mu$ on a Beckman DU spectrophotometer equipped with a photomultiplier. An aliquot of the reaction mixture was withdrawn and its absorbance measured within 1 min. The time noted was the time at which the actual reading was made.

The absorbance of a solution of thiobenzoic acid under the reaction conditions was found to increase gradually over a period of several days. The absorbance of the reaction mixture showed a similar increase after the completion of the reaction. The amount of this increase was observed to be about 8% in the first 24 hr. The infinity readings for the kinetic runs were taken after 24 hr. Therefore, an 8% correction was made on all of the infinity readings.

Two determinations of the rate constant were made in 0.20 *M* sodium hydroxide using a Cary Model 14 spectrophotometer with a thermostated jacket held at 25.0°. At this base concentration the solvent begins to turn noticeably yellow after about 5 min.

Titrations.—The rate of hydrolysis of ethyl benzoate in base was determined by titrating unchanged base in aliquots withdrawn during the course of a run. The aliquot was added to a beaker containing about 25 ml. of pentane and 25 ml. of water contain-

ing almost enough acid to neutralize the remaining base. It was shown that use of this procedure stops the reaction completely. Cresol red was used as indicator.

The runs in acid were done by a similar procedure, except that the formation of benzoic acid was followed by noting the increase in titer with time. Two of the runs in acid were done by plotting the titration curve for each aliquot on a Polared automatic titrimeter, Model AT-2A. The results of these determinations did not differ significantly from the determinations by direct titration.

Gas Chromatography.—The concentrations of ethyl benzoate and ethyl thionbenzoate were followed during the course of a reaction by gas chromatography. In the runs in base, an aliquot of the reaction mixtures was added to a mixture of about 25 ml. of pentane and 25 ml. of water, to which an aliquot of a standard solution of 2,4-dimethylacetophenone had been added as an internal standard. The pentane layer, containing the two esters and the internal standard, was concentrated to about 0.1 ml. and chromatographed on an Aerograph Hy-Fi gas chromatograph equipped with a hydrogen-flame detector. The column used was 20% Carbowax on Chromosorb W, 3 ft. long and 1/8 in. in diameter.

The same chromatographic procedure was followed for the determinations in acid solution, except that carbon disulfide was used instead of pentane, sodium bicarbonate was added to the water in order that the benzoic and thiobenzoic acids would not be extracted into the organic layer, and *m*-nitrotoluene was used as the internal standard.

Ion-Radicals. III.¹ The Isolation of a Hydroxythianthrene Oxide from Thianthrene Monoxide in Concentrated Sulfuric Acid

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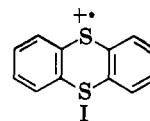
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A hydroxythianthrene oxide II has been isolated from the cyclohexane-insoluble, tan solid obtained by pouring solutions of thianthrene monoxide in 96% sulfuric acid onto ice. Reduction of this oxide by tin in acetic acid gave 2-hydroxythianthrene. The oxide II in 96% sulfuric acid undergoes reactions which are analogous to those of thianthrene oxide. That is, II is converted to an ion-radical whose electron spin resonance, ultraviolet, and visible spectra are similar to those obtained from 2-hydroxythianthrene in 96% sulfuric acid.

When thianthrene monoxide dissolves in concentrated sulfuric acid it undergoes, in part, a transformation to thianthrene.³ This transformation is accompanied by a change in the color of the solution, from amber to purple. Similar color changes are observed with solutions of thianthrene *cis*-5,10-dioxide.³ Further, somewhat related transformations occur when these two oxides are suspended in concentrated hydrochloric acid.^{3,4} Recent investigations⁵⁻⁷ have shown that these transformations are associated with the formation of a radical. It has been shown that this radical is the same as that obtained from solutions of thianthrene in sulfuric acid,^{5,6,8} and from solutions of thianthrene containing aluminum chloride.⁶ Solutions of the radical give rise to a symmetrical five-line e.s.r. spectrum, not

only in sulfuric acid but also in hydrochloric acid.⁹ This spectrum and other data have led to the proposal^{6,8} that the solutions contain the ion-radical I.



It was shown in our earlier work⁶ that, whereas the pouring of solutions of thianthrene in sulfuric acid onto ice gave only thianthrene and its monoxide as products, similar treatment with the monoxide gave thianthrene, the monoxide, and a tan solid. It was noted that the composition of the tan solid, although unknown, appeared to vary with the length of time the sulfuric acid solution was kept before pouring onto ice. The formation of both thianthrene and the tan solid and the shape of the e.s.r. spectrum obtained from a solution of the tan solid in sulfuric acid, led to the proposal⁶ that the tan solid was a hydroxythianthrene oxide. The transfer-hydroxylation of one molecule of thianthrene oxide was proposed as a mode by which the reduction of a second, protonated, molecule of monoxide could occur.

(9) C. F. Dais, unpublished experiments to be used as part of a Ph.D. thesis at Texas Technological College. In a subsequent contribution we shall deal in detail with the reactions of, and trapping of intermediates from, thianthrene monoxide in concentrated hydrochloric acid.

(1) (a) Part IV, H. J. Shine, C. F. Dais, and R. J. Small, *J. Org. Chem.*, in press; (b) We are grateful for the generous support of parts of this work by the Robert A. Welch Foundation and the Directorate of Chemical Sciences, Air Force Office of Scientific Research (grant no. AF-AFOSR-23-63).

(2) Post-doctoral Fellow, 1961-1962.

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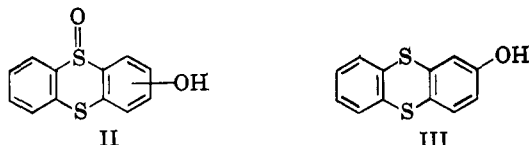
(7) H. J. Shine, C. F. Dais, and R. J. Small, *J. Chem. Phys.*, **38**, 569 (1963).

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We now wish to report the isolation of a hydroxythianthrene oxide as a component of the tan solid and the behavior of this oxide in sulfuric acid solution.

Results

Isolation.—The oxide II was isolated from solutions of thianthrene monoxide in 96% sulfuric acid which had been standing for 165 minutes and 129 hours.



These times were chosen on the basis of our earlier results⁶ in following the change in solution spectroscopically. The precipitates obtained from each of these solutions were treated to remove thianthrene and thianthrene monoxide and then extracted with sodium hydroxide solution. Carbonation of the alkaline solutions gave the product II. The greater amount of II was obtained from the acid solution which had been kept for 165 minutes. This is in accord with some of the earlier speculations⁶ and with the reactions of II in sulfuric acid, which we now have investigated briefly. The compound II is crystalline and colorless and has a melting point of 244–245°. The position of the hydroxyl group is unknown. Reduction of II by tin in acetic acid gave 2-hydroxythianthrene (III) found to be identical with an authentic specimen.

Absorption Spectra.—The oxide II dissolves rapidly in 96% sulfuric acid. Like thianthrene monoxide, II in 96% sulfuric acid undergoes a transformation which is accompanied by a change in the color of the solution. The change can be followed by both the ultraviolet and the visible spectra, and after the change has occurred the spectra of the solutions correspond with those of 2-hydroxythianthrene in 96% sulfuric acid. The ultraviolet spectrum of II in sulfuric acid initially has a band at 292 m μ and a larger, slender band at 319 m μ which disappears in time and is replaced by an increase in absorption at 292 m μ . Over much of the time the changing spectra go through an isosbestic point at 300 m μ . This change is shown in Fig. 1. The ultraviolet spectrum of 2-hydroxythianthrene in 96% sulfuric acid is included in Fig. 2, while in Fig. 3 are shown the visible spectra of 2-hydroxythianthrene and II in 96% sulfuric acid.

The rate at which II changed in 96% sulfuric acid was found, qualitatively, to be a function of the concentration of II. That is, a 1.6×10^{-5} M solution of II was found to have changed much more extensively after 25 hours than a 1.6×10^{-5} M solution of II made by freshly diluting a 8×10^{-5} M solution which had been standing for 25 hours. This difference is shown in Fig. 2.

E.s.r. Spectra.—A solution of II in 96% sulfuric acid showed a strong e.s.r. spectrum as soon as it was prepared. The shape of the spectrum did not change with time but the intensity increased. The e.s.r. spectrum appeared to be identical with one obtained from a solution of III in 96% sulfuric acid.

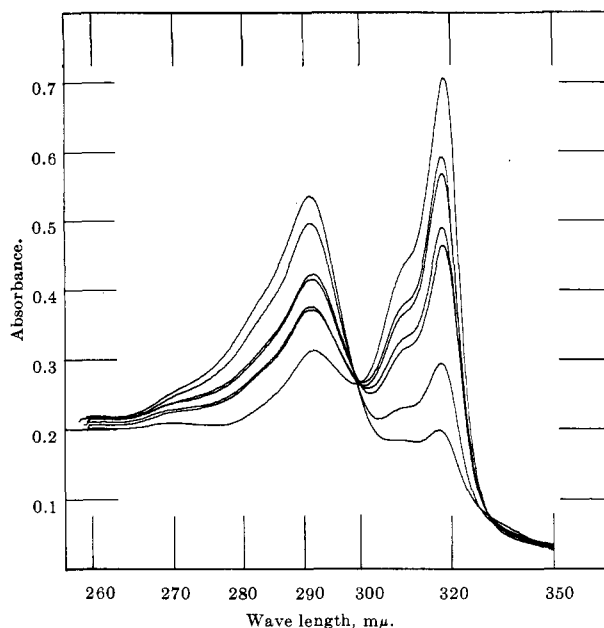


Fig. 1.—The change in time in the ultraviolet spectrum of a 1.6×10^{-5} M solution of II in 96% sulfuric acid. The time intervals, from the time of dissolving until the time of starting the seven scans, were 20, 70, 80, 120, 625, and 1245 min.

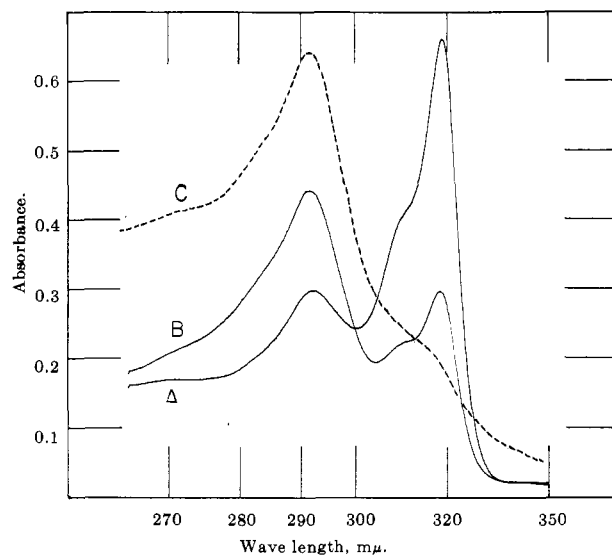


Fig. 2.—Ultraviolet spectra in 96% sulfuric acid: A, a 1.6×10^{-5} M solution of II freshly made from an 8×10^{-5} M solution of II which had been standing for 25 hr.; B, a 1.6×10^{-5} M solution of II which had been standing 25 hr.; C, 2-hydroxythianthrene.

Discussion

The isolation of a hydroxythianthrene oxide from a solution of thianthrene monoxide in 96% sulfuric acid is in accord with our earlier proposals⁶ about the ways in which thianthrene monoxide may be converted to the ion-radical I. Although the exact structure of the oxide II is not known, it can be only either 2- or 3-hydroxythianthrene 5-oxide, since reduction of the sulfoxide group gave 2-hydroxythianthrene.

In our earlier work⁶ we classified as "tan solid" those products which were insoluble in cyclohexane at room temperature. It is now understandable that the insolubility results from the substitution of the phenolic hydroxyl group in the already poorly soluble monoxide, so that the earlier⁶ division of products was the result

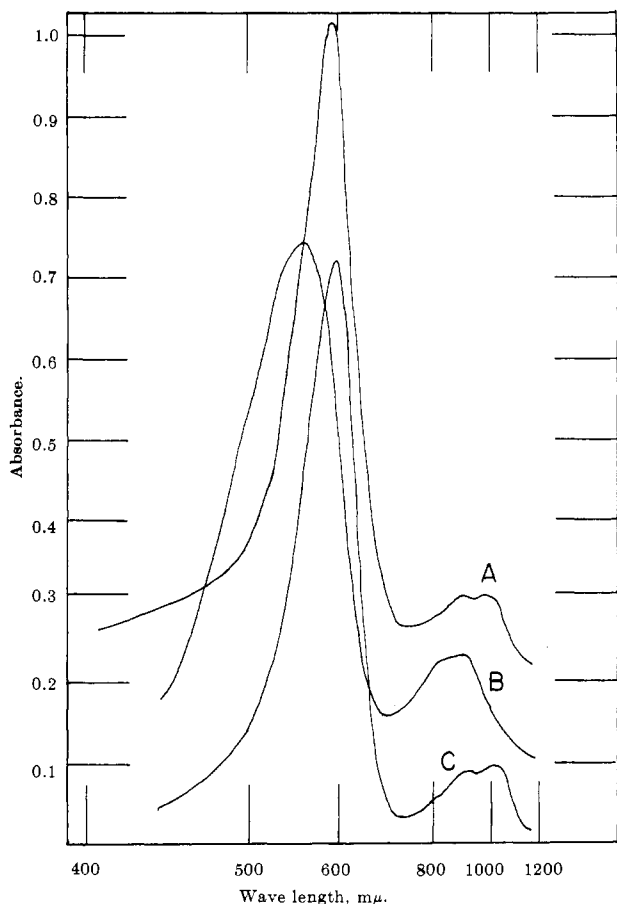
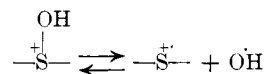


Fig. 3.—Visible spectra in 96% sulfuric acid: A, a 20-day old solution of II; B, a freshly made solution of II; C, 2-hydroxythianthrene. Curves A and B have been raised 0.2 and 0.1 in absorbance for clearer presentation.

of a fortunate, circumstantial choice of extraction solvent. The oxide II does not constitute all of the tan solid, however. We have been able to separate a second phenolic compound from experiments in which thianthrene monoxide remained many days in 96% sulfuric acid. Unfortunately, we have been unable to purify this compound satisfactorily, so that further comment on its nature must be postponed. The presence of more than one hydroxy compound in the tan solid is also in accord with our earlier observations.⁶

The oxide II undergoes a transformation in 96% sulfuric acid which is analogous to the case of thianthrene monoxide. In the new example the transformation appears to be to the ion-radical characteristic of 2-hydroxythianthrene in 96% sulfuric acid.¹ The absorption curves recorded in Fig. 2 disclose an important feature in this class of transformations. The change from II to the ion-radical becomes faster if the initial concentration of the II is lowered. We have observed the same feature with thianthrene monoxide and a more detailed study of the monoxide is being made. This increase in rate and the well defined isobestic points that appear in the spectra of changing thian-

threne monoxide⁶ and in Fig. 1, suggest that the conversion of these oxides to the ion-radical is a one-step reversible dissociation, rather than a bimolecular hy-



droxyl-transfer reaction.⁶ Discussion of this feature will be postponed for a later publication (part V) and correlated with our recent results with thianthrene monoxide, the conflicting reports^{5,6} about Beer's Law in these systems, and the behavior of thianthrene monoxide in trifluoroacetic acid.^{5,6,8}

Experimental¹⁰

Isolation of a Hydroxythianthrene Oxide (II).—A solution of 2.32 g. (0.01 mole) of thianthrene monoxide in 500 ml. of 96% sulfuric acid was prepared. After 165 min. half of this solution was poured onto ice. A precipitate (A) formed and was removed next day by filtration. The remaining half of the acid solution was poured onto ice after standing 129 hr. The precipitate (B) was filtered similarly. After washing with water and drying, the light tan A weighed 1.05 g. and the dark tan B weighed 1.07 g.

Each of these solids was subjected to continuous extraction by hot cyclohexane in a Soxhlet extractor to remove thianthrene and thianthrene monoxide completely. The dried, cyclohexane-insoluble residues weighed 0.301 g. (A-1) and 0.357 g. (B-1). The A-1 and B-1 were separately shaken for 6 hr. with dilute aqueous potassium hydroxide solution. The filtered solutions were treated with gaseous carbon dioxide and the precipitates formed were removed by filtration, washed, and dried to give 0.211 g. (A-2) and 0.109 g. (B-2) of almost colorless solids. Each was crystallized from methanol; the B-2 solution was heated with activated charcoal. Colorless needles were obtained with m.p. 244–245° (A-2) and m.p. 244–250° (B-2). The A-2 was analyzed.

Anal. Calcd. for C₁₂H₈O₂S₂: C, 58.07; H, 3.25; S, 25.79. Found: C, 58.25; H, 3.31; S, 26.00.

The infrared spectrum (potassium bromide pellet) showed a sharp sulfoxide¹¹ absorption at 1041 cm.⁻¹ similar in shape (small shoulder at 1025–1030 cm.⁻¹) to the sulfoxide band, 1038 cm.⁻¹, obtained with thianthrene monoxide.

2-Hydroxythianthrene (III).—Earlier experiments had shown that thianthrene monoxide could be reduced cleanly to thianthrene by boiling with zinc and acetic acid. Therefore, 25 mg. of the hydroxy sulfoxide, B-2, was boiled for 4 hr. with 4 ml. of acetic acid and some zinc granules. Filtration of the hot solution and removal of the solvent under reduced pressure gave 17 mg. of residue, m.p. 142°. Crystallization from aqueous methanol gave slightly yellow plates, m.p. 144–145°. The infrared spectrum of the product was identical with that of authentic 2-hydroxythianthrene, m.p. 143°, prepared from 2-bromothianthrene¹² by the method of Pützer and Muth,^{13,14} lit.¹³ m.p. 145°.

Spectra.—The ultraviolet and visible spectra were obtained with a Beckman Model DK-2 recording spectrophotometer. The e.s.r. spectra were obtained with a Varian Associates spectrometer using 100-kc. field modulation, and Varian Associates flat, quartz cells.

(10) Analyses by Schwarzkopf Microanalytical Laboratories, Woodside, Long Island, N. Y.

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(14) We are grateful to Mr. C. N. Sechrist, American Oil Co., Texas City, Tex., for carrying out the high pressure hydrolysis.