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THE FORMATION OF THE THIOXANTHYLIUM ION FROM THIOXANTHENE 10-OXIDE IN CONCENTRATED SULFURIC ACID AND FROM DITHIOXANTHYL.

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The reactions which aromatic sulfoxides may undergo in strong acids have been discussed in earlier papers of this series (1,2). The reactions may be summarized by the equations 1 and 2. Whether equation 2 shows the correct stoichiometry

$$R_2S{=}O \overset{H^+}{\rightleftarrows} R_2\overset{+}{S}{-}OH \overset{H^+}{\rightleftarrows} R_2S^{\ddagger} + H_2O \qquad (1)$$

$$R_2\overset{+}{S}{-}OH \xrightarrow{(-OH)} R_2S^{\overset{+}{\cdot}} \qquad (2)$$

for cation-radical formation cannot be said. To what extent a sulfoxide can participate in these reactions depends on the structure of the sulfoxide and the strength of the acid. Some sulfoxides, for example diphenyl sulfoxide and certain substituted diphenyl sulfoxides, have been shown not to go beyond the monoprotonated stage in concentrated sulfuric acid (3-5).

As for the dehydroxylation of a monoprotonated sulfoxide (equation 1), only recently have O^{18}-labelling and *i*-factor

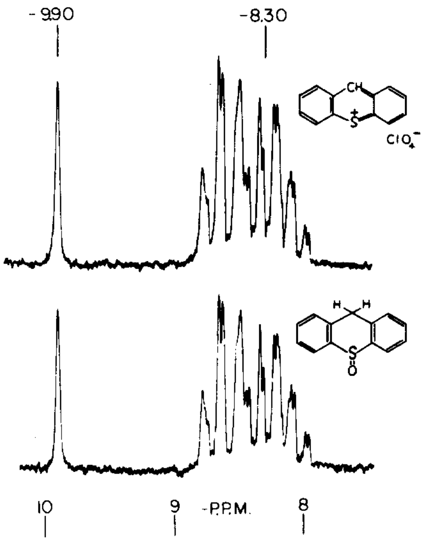


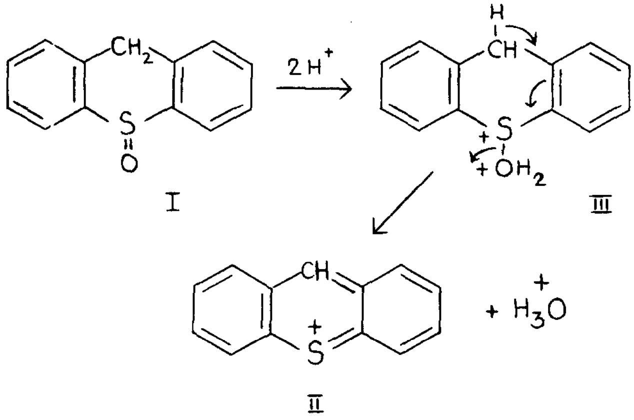
Fig. 1. N.m.r. spectra of thioxanthylium perchlorate and thioxanthene 10-oxide in 96% sulfuric acid. The p.p.m. scale refers to tetramethylsilane as 0.

data with thianthrene 5-oxide in 100% sulfuric acid given evidence of its occurring (6). The dehydroxylation reaction has been inferred from work with phenothiazine 5-oxide (1) and phenoxathiin 5-oxide (2), but proof was not provided.

We have now obtained further evidence for the dehydroxylation reaction by using thioxanthene 10-oxide (I). Thioxanthylium perchlorate was prepared from thioxanthene-9-ol by the method of Price and co-workers (7). The n.m.r. spectrum of the perchlorate in 96% sulfuric acid is shown in Fig. 1. The n.m.r. spectrum of I in 96% sulfuric acid is also shown in Fig. 1, and is seen to be identical with that of thioxanthylium perchlorate. Tetramethylammonium chloride was used as an internal standard (8). The standard gave a single peak 3.11 p.p.m. downfield from tetramethylsilane. The single peak at -9.90 p.p.m. (with respect to tetramethylsilane) in each spectrum in Fig. 1 is attributable to the benzylic hydrogen of the thioxanthylium ion (II), while the overlapping multiplets due to the ring protons are centered at -8.30 p.p.m.

The probable mechanism of the formation of II from I is shown in Sequence A, and conforms in principle with equation 1. The deprotonation and dehydration of the intermediate (III) are written as concerted steps only for convenience. We know no detail about the time sequence of these steps. The formation of II from I in concentrated sulfuric acid requires an <u>i</u>-factor of 4 (equation 3). <u>i</u>-Factor determinations were carried out

$$\mathrm{I} + 2H_2SO_4 \rightarrow \mathrm{II} + H_3\overset{+}{O} + 2HSO_4^- \qquad (3)$$



Sequence A

in slightly aqueous sulfuric acid using incremental additions of the solute as described earlier (6). A cryoscopic constant of 6.12 was used in the calculations (9). The data are given in Table I and support the proposal for the formation of II.

Thus, both the n.m.r. and i-factor data are consistent with the proposal that an aromatic sulfoxide may be deoxygenated after having become diprotonated by a strong acid.

The reactions in equation 1 are written as being reversible. The hydration of the thianthrene dication does indeed

Table I

$\underline{i}$-Factor Data for Solutions of Thioxanthene 10-Oxide in Sulfuric Acid.

Sample Weight, g.	Molality x 10^3	f. pt., °C	ΔT, °C	Time, hr.	$\underline{i}$
0	-	9.187	-	-	-
0.2294	5.786	9.047	0.140	1	3.97
0.4505	11.36	8.905	0.282	13	4.08
0.6738	16.99	8.770	0.417	25	4.03
0.9100	22.95	8.628	0.559	49	4.00
1.1195	28.24	8.485	0.702	67	4.08

reform thianthrene 5-oxide (6). The hydration of the thioxanthylium ion, however, occurs at the 9-carbon, not the sulfur, atom. Thioxanthene and thioxanthenone are formed, probably by a combination of hydride transfer between the thioxanthylium ion and thioxanththenol and some air oxidation of thioxanthenol. Similar observations have been made by Fields and Meyerson (10) with the hydrolysis of thioxanthylium perbromide. In connection with the last work, we have found that the reaction of the dimer, dithioxanthyl, with bromine gives thioxanthylium perbromide quantitatively rather than dithioxanthylium perbromide as reported (10,11). Dithioxanthyl is also converted quantitatively into the thioxanthylium ion in concentrated sulfuric acid.

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This paper is considered to be Part IX in the series on ion radicals.

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11. Dr. Fields has kindly informed us that he has confirmed our observation.