

ION RADICALS. VIII. THE THIANTHRENE
DICATION IN SULFURIC ACID

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A number of aromatic sulfides and sulfoxides dissolve in sulfuric acid to produce highly colored solutions, and it is a matter of considerable interest to know what species are responsible for the colors. This is particularly true with sulfoxides. In some cases a sulfoxide is converted to a cation radical in concentrated sulfuric acid. In these cases it is thought that the cation radical arises from the first-formed, protonated sulfoxide, $\text{Ar}_2\overset{+}{\text{S}}\text{OH}$, and that the color eventually achieved by the acid solution is due to the cation radical. Where an oxide is not converted to a cation radical, but nevertheless causes an acid solution to be colored, it is thought generally that the color is due to the stable, protonated oxide. The additional possibility that a protonated sulfoxide may be dehydroxylated to a dication in strong acid solution (equation 1) is very attractive. Some years ago it was

proposed (1) that the green color of diphenyl sulfoxide (I)



in 100% sulfuric acid was caused by the dication, Ph_2S^{++} .

Other workers have found this proposal not to be correct and have shown, instead, by freezing-point measurements (2) and O^{18} -labelling (3,4) that diphenyl sulfoxide in 97% and 100% sulfuric acid exists only as the protonated oxide.

Although the dehydroxylation of the protonated sulfoxide has not been found to occur in diaryl sulfoxides (2-4) it does appear to occur in some heterocyclic sulfoxides. Work with phenothiazine 5-oxide (5) and phenoxathiin 5-oxide (6) has led to the conclusion that these oxides are converted to dications in sulfuric acid solution as in equation 1. Tests for dication formation can be made by drowning the sulfuric acid solution with H_2O^{18} , in which case O^{18} would become incorporated in the reformed sulfoxide, and by μ -factor measurements. It is not easy to make an O^{18} -labelling test for the formation of dications from phenothiazine- and phenoxathiin 5-oxide, because of the reactions these oxides undergo in aqueous-acid solutions (5,6). However, the test can be made with thianthrene 5-oxide (II), because solutions of this oxide in 100% sulfuric acid are very stable and precipitate the oxide immediately when poured onto ice (7).

We have tested for dication formation by pouring 5-minute old solutions of II (11.6 mg.) in 100% sulfuric acid (5 ml.) onto ice (50 g.) made from O^{18} -enriched water. This treatment caused the immediate precipitation of II, whose O^{18} -content was found to be close to the theoretical for the reversal of equation 1. The O^{18} -content of the precipitated II was determined from the mass spectrum of the II (8). Control experiments were made with solutions of II in 100% sulfuric acid that were poured onto ordinary ice. A further control run and test of the analytical method was made by similarly treating diphenyl sulfoxide (I) in 96% sulfuric acid. It has already been shown by the conversion-to-carbon-dioxide method that O^{18} -enrichment does not occur in this case and that the dication is not formed (3). [96-97% sulfuric acid is used with this sulfoxide because the recovery from 100% acid solutions has been found by others (4), and confirmed by us, to be very poor.] The direct mass measurements with I also show that enrichment does not occur.

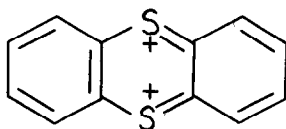
The results for I and II are given in Table I in terms of the relative height of the $(m + 2)/e$ peak in the mass spectrum, the relative height of the peak m/e for the unenriched molecule being taken as 100. The calculated values were obtained as described by Beynon (9). The results are consistent with the conversion of II to the dication III, and the

Table I
Relative Height of Peak of Mass (m + 2) in the
Mass Spectrum of Precipitated Sulfoxides

Source of Ice	I, (m + 2)/e = 204		II, (m + 2)/e = 234	
	Exptl.	Calcd.	Exptl.	Calcd.
H ₂ O ¹⁸ *	5.5 ± .05	7.3	11.4 ± .2	11.7
H ₂ O ¹⁶	5.5 ± .04	5.6	10.0 ± .2	10.1

*enrichment 1.7%

hydroxylation of III by pouring onto ice.



III

The results are also consistent with the possibility that II in sulfuric acid solution exists only as protonated II rather than III, and that the incorporation of O¹⁸ in the recovered II came from the rapid exchange between H₂O¹⁸ and the protonated II at the time of precipitation of the II. If this were the mode of O¹⁸ incorporation in II, we would have to conclude from the absence of O¹⁸ incorporation in I either that I is unprotonated in 96% sulfuric acid or that I is protonated but protonated I does not suffer the exchange reaction with H₂O¹⁸.

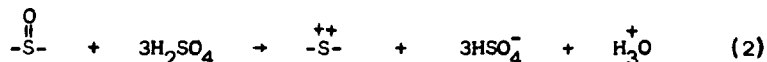
These requirements make the exchange mode of O^{18} incorporation in II seem improbable. The point is settled by \underline{i} -factor determinations, which support the proposal for dication formation.

The \underline{i} -factor determinations were made with slightly aqueous sulfuric acid solutions. Freezing points (Table II) were obtained after making incremental additions of II to the acid.

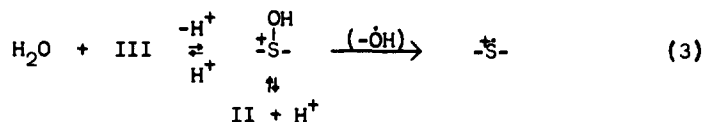
Table II
 \underline{i} -Factor Data for Solutions of
Thianthrene 5-Oxide in Sulfuric Acid

Sample Weight, g.	Molality $\times 10^3$	f. pt., $^{\circ}C$	ΔT , $^{\circ}C$	Time, hr.	\underline{i}
0	0	10.266	0	0	-
0.2207	5.00	10.110	0.156	24	5.09
0.4360	9.88	9.963	0.303	48	5.01
0.6585	14.92	9.810	0.456	56	4.99
0.8989	20.36	9.640	0.626	68	5.02
1.3329	30.19	9.330	0.936	140	5.06

An apparatus similar to that described by Gillespie (10) was used, except that a -1 to 11° thermometer instead of a thermocouple was incorporated. The freezing points were steady over long periods of time, and the \underline{i} -factor was not affected by changing the concentrations of II. An \underline{i} -factor of 5 is required for the dehydroxylation reaction (equation 2).



Solutions of II in 100% sulfuric acid have absorption maxima at 311 and 502 $m\mu$. In a previous paper (7) one of us described the formation of the thianthrene cation radical from II in 96% sulfuric acid. The ultraviolet and visible spectra of solutions of II in this acid changed with time, and the changes were due to the formation of the cation radical. For example, the ultraviolet spectrum changed from having a maximum at 311 $m\mu$ to having maxima at 270 and 290 $m\mu$. The nature of the species absorbing at 311 $m\mu$ was not known then, but was described as probably being the protonated oxide. It can be seen now that this species is the dication. The route from II to the thianthrene cation radical in 96% sulfuric acid is now better described by the equation 3, the detail of which has been discussed for the related



cases of phenothiazine- and phenoxathiin 5-oxide (5,6).

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