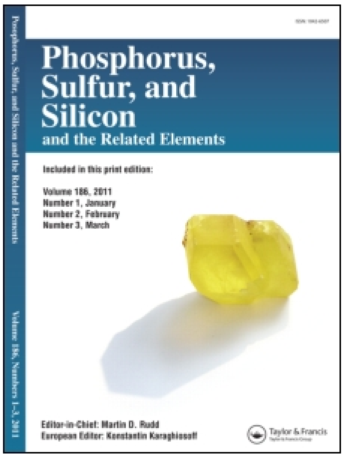

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HOW SULFOXIDES (S=0) BECOME CATION RADICALS (S+) IN ACID SOLUTIONS. A RE-ASSESSMENT

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HOW SULFOXIDES ($>S{=}O$) BECOME CATION RADICALS ($>S^{\bullet +}$) IN ACID SOLUTIONS.

A RE-ASSESSMENT

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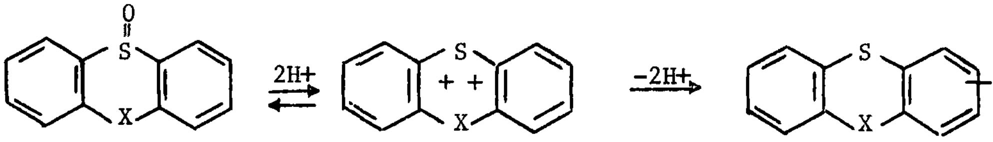
It has been known for many years that heterocyclic sulfoxides [e.g., phenothiazine- (**1**), thianthrene- (**2**), and phenoxathiin 5-oxide (**3**)] are converted into the parent cation radicals in acid solution. The same reaction occurs with $(XC_6H_4)_2S{=}O$ in which X is an electron-donating group. This behaviour has been represented for years as the homolysis of the protonated (or diprotonated) sulfoxide (eqs. 1,2).

$$>S{=}O + H^+ \qquad >\overset{+}{S}{-}OH \rightarrow >S^{\bullet +} + {}^{\bullet}OH \qquad (1)$$

$$>\overset{+}{S}{-}OH + H^+ \qquad >\overset{+\,+}{S{-}OH_2} \rightarrow >S^{\bullet +} + H_2O^{\bullet +} \qquad (2)$$

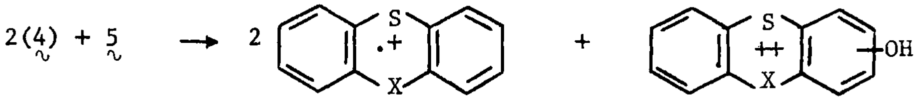
Some years ago it was shown that each of the heterocyclic 5-oxides gave, in fact, two cation radicals in acid solution. For example, **1** in 59% H_2SO_4 gave both phenothiazine- and 3-hydroxyphenothiazine cation radical (Shine and Mach, 1965). Similar results were obtained with **2** (Shine and Piette, 1962; Shine and Robinson, 1963) and **3** (Shine and Small, 1965) in 96% H_2SO_4. The formation of the parent cation radical appeared, spectroscopically, to originate from the heterocyclic dication, while the formation of the hydroxy cation radical appeared to occur later than that of the parent.

These reactions are now re-evaluated and explained without resorting to homolytic pathways. It is proposed that the dication is hydroxylated at a ring position (e.g., eq. 3), and that the hydroxy heterocycle so formed reduces more of the dication to the cation radical (e.g., eq. 4). In so doing a hydroxy dication is formed, which itself is reduced in subsequent similar reactions. An example is given in eqs. 3-5, using 2 (X = S) and 3, X = O. Modification is needed for 1 (X = NH) since the dication in its deprotonated form is involved (cf. Hanson and Norman, 1973). Spectroscopic evidence for these proposals is presented.



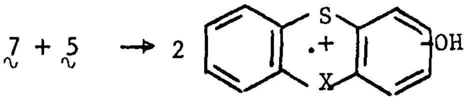
(3)

4 + $2H_2O$ 5



(4)

6 7



(5)