Tetrahedron Letters No.50, pp. 5255-5258, 1968. Pergamon Press. Printed in Great Britain.

CATION RADICALS FROM ORGANOSULFUR COMPOUNDS IN PERSULFURIC ACID SOLUTION. (1,2)

H. J. Shine, M. Rahman, H. Nicholson and R. K. Gupta

Department of Chemistry, Texas Technological College, Lubbock, Texas 79409.

(Received in USA 19 June 1968; received in UK for publication 9 September 1968)

The formation of sulfinium ions from aromatic thioethers and certain heterocyclic sulfur compounds by one-electron oxidation with concentrated sulfuric acid and the formation of the same ions by deoxygenation of the corresponding sulfoxides in concentrated sulfuric acid are well established (3). There are reports in the literature that the same sulfinium ions are also obtained from the sulfides and heterocyclic sulfur compounds by oxidation with potassium persulfate in concentrated sulfuric acid. Thus, a series of diphenyl sulfides have been reported as giving the corresponding diphenylsulfinium ions when dissolved in either concentrated sulfuric acid or in concentrated sulfuric acid containing potassium persulfate (4). A similar result has been reported for phenoxathiin (5). Two differences between our work with sulfuric acid and the reported work with potassium persulfate/sulfuric acid prompted us to study the reactions of organosulfur compounds in potassium persulfate/sulfuric acid solution. One of the discrepancies was our observation several years ago that the thianthrene cation radical was short-lived in solutions of potassium persulfate/sulfuric acid. Depending on the amount of potassium persulfate used the molecule was converted to the tri- or tetra-S-oxide. Each of these compounds could be obtained in excellent yield as desired. The other discrepancy was between our characterization of the di-p-tolylsulfinium ion (7) and Schmidt's (5,8). We had found that the di-p-tolylsulfinium ion, formed either from p-tolylsulfide or p-tolylsulfoxide in concentrated sulfuric acid had an esr spectrum with 15 major lines split into overlapping multiplets. The g-value for the radical was 2.00737 and its solutions were blue-green. The radical was not long-lived in concentrated sulfuric acid. Schmidt reported a red color for the radical's solution, and a 7-line spectrum with a g-value of 2.0091. Our own observations have since been confirmed by Oae (9). We do not know the reason for the g-value of 2.0091 obtained by Schmidt.

We are now able to report that sulfinium ions are not formed from aromatic sulfides in potassium persulfate/concentrated sulfuric acid solution; or, if formed, they have very short lives. Radicals are detectable (presumed to be cation radicals), but in our opinion they are the radicals of more extensively oxidized molecules.

The data in Tables 1 and 2 (obtained with substrate:persulfate molar ratios of 1:3) show that radicals are obtained not only from aromatic sulfides but also from sulfoxides, sulfones and sulfonic acids. The last two types of compound are not ordinarily attacked by concentrated sulfuric acid alone.

Tables 1 and 2 show the very important fact that the g-values of radicals obtained with potassium persulfate/sulfuric acid are low. The g-values of aromatic sulfinium ions fall in the range 2.007 - 2.01 (3). This range of relatively high values is attributable to spin-orbit coupling at the sulfur atom. It is evident that this type of coupling cannot be important in the radicals obtained with the use of potassium persulfate. Thus, apart from any differences in hyperfine lines and colors of solutions, it becomes evident from the difference in g-values that the radicals obtained in potassium persulfate/sulfuric acid solutions cannot be the sulfinium ions.

It is our feeling that the radicals with low g-values are those of hydroxylated molecules. It has already been shown with aromatic hydrocarbons such as p-xylene (10) that the cation radical obtained in potassium persulfate/sulfuric acid is not the parent monocation but the cation radical of the corresponding hydroquinone. That is, the persulfuric acid dihydroxylates the aromatic ring before the final one-electron oxidation occurs. It appears to us that persulfuric acid in concentrated sulfuric acid is such a powerful electrophile that

Table 1

g-Values of Organosulfur Radicals in H_2SO_4 and $H_2SO_4/K_2S_2O_8$

	H_2SO_4		$H_2SO_4/K_2S_2O_8$	
Substrate	lines	g	lines	g
p-Tolylsulfide	15*	2.00737	13	2.00336
p-Tolylsulfoxide	15*	2.00738	13	2.00337
p-Tolylsulfone	-	-	complex	2.00354
Methyl p-tolyl sulfoxide	13	2.00818	7	2.00351
Methyl p-tolyl sulfone	-	-	17	2.00375

---

*Split further into overlapping multiplets.

Table 2

g-Values of Organosulfur Radicals in $H_2SO_4/K_2S_2O_8$

Substrate	lines	g
2-Hydroxy-4,4'-dimethylphenyl sulfone	21	2.0035
Phenyl sulfone	3-6	2.0036
2-Hydroxyphenyl phenyl sulfone	3-6	2.0035
2,5-Dihydroxyphenyl phenyl sulfone	5	2.0036
Hydroquinone-2,5-disulfonic acid	3	2.0035
Biphenyl-4,4'-disulfonic acid	3-5	2.0037

it even hydroxylates sulfones and sulfonic acids (via the first-formed sulfate ester groups).

The range of g-values (2.0035 - 2.0037) is consistent with the proposal that hydroxyl groups are in an aromatic ring of a radical. Norman and Gilbert (11) have commented on the g-values of aromatic radicals containing a hydroxyl group. The range of low g-values in Tables 1 and 2 also indicates little, if any, unpaired-electron density on the sulfur atom(s) of the radicals. This suggests to us that dihydroxylation has occurred in one ring only of the diaryl substrates and that the unpaired electron is confined to that ring.

Another difference between the sulfuric acid and potassium persulfate/sulfuric acid systems is worth pointing out. An aromatic sulfoxide with appropriate substituents in sulfuric acid will give a sulfinium ion (7); that is the sulfoxide loses its S-oxygen atom. In contrast, it appears to us that in potassium persulfate/sulfuric acid a sulfide is first oxidized to the sulfoxide and next converted to the same radical as obtained directly from the sulfoxide. Thus, the radical obtained from p-tolylsulfide and p-tolylsulfoxide is, we believe, that of the dihydroxylated sulfoxide. It is apparent from Table 1 that a diaryl sulfoxide is not oxidized further to the sulfone, which is understandable since the sulfoxide is probably completely protonated (on oxygen) in the strongly acidic medium.

We thank the Directorate of Chemical Sciences, Air Force Office of Scientific Research, for generous support under Grants AF-AFOSR-975-66 and AF-AFOSR-68-1359.

References

(1) Part XV in a series. Part XIV: H. J. Shine and P. D. Sullivan, J. Phys. Chem., 72, 1390 (1968).

(2) This work was described at the 3rd International Organosulfur Symposium, Caen, France, May 21, 1968.

(3) H. J. Shine, in Organosulfur Chemistry, Reviews of Current Research, ed. M. J. Janssen, Wiley, New York, 1967, pp. 93-117.

(4) U. Schmidt, K. Kabitzke, K. Markau, and A. Müller, Ann., 672, 78 (1964).

(5) U. Schmidt, K. Kabitzke, and K. Markau, Ber., 97, 498 (1964).

(6) Unpublished work of Dr. T. A. Robinson, 1962.

(7) H. J. Shine, M. Rahman, H. Seeger, and G.-S. Wu, J. Org. Chem., 32, 1901 (1967).

(8) U. Schmidt, Angew. Chemie Intl. Edn., 3, 602 (1964).

(9) S. Oae and N. Kunieda, Bull. Chem. Soc. Japan, 41, 696 (1968).

(10) J. A. Brivati, R. Hulme and M. C. R. Symons, Proc. Chem. Soc., 384 (1961); J. R. Bolton and A. Carrington, ibid, 385 (1961).

(11) R. O. C. Norman and B. C. Gilbert, in Advances in Physical Organic Chemistry, Vol. 5, ed. V. Gold, Academic Press, 1967, p. 92.