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THE SULFUR ANALOG OF WURSTER'S BLUE CATION-RADICAL[1]

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N,N,N'N'-Tetramethyl-p-phenylenediamine (I) is known to undergo one-electron oxidation under a variety of conditions(2) to the corresponding cation-radical, a blue substance, which has absorption maxima at 621 mμ and 571 mμ (3) The e.s.r. derivative spectrum of the cation-radical of I has been extensively examined,(4) and the hyperfine coupling constants have been found to be $a_N = 6.99$ gauss, $a_{CH_3} = 6.76$ gauss, and $a_H = 1.97$ gauss.

We wish to report here the analogous(5) one-electron oxidation of the known dithiohydroquinone dimethylether (II).(6) In 96% sulfuric acid II also gave deep blue solutions ($\lambda_{max.}$ at 787 mμ, 725 mμ (sh), and 615 mμ) with strong e.s.r signals. The e.s.r. pattern of these solutions showed many lines apparently due to the presence of more than one species, however a dominant pattern

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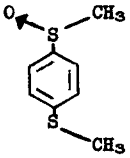
(1) Cumulative Influence of Conjugated Substituents on the π-System Properties of Aromatic Hydrocarbons, V. To be published.
(2) L. Michaelis, M. P. Schubert and S. Granick, J. Am. Chem. Soc., 61, 1981 (1939).
(3) R. Foster and T. J. Thomson, Trans. Faraday Soc., 58, 860 (1962).
(4) J. R. Bolton, A. Carrington and J. dos Santos-Veiga, Mol. Phys., 5, 615 (1962).
(5) Many analogies in the chemical properties of divalent sulfur and trivalent nitrogen compounds and their derived cations are known. cf. F G. Bordwell and P. J. Boutan, J. Am. Chem. Soc., 78, 87, (1956).
(6) T. Zincke and W. Frohneberg, Ber. Dtsch. Chem. Ges., 42, 2721 (1909).

of seven groups of evenly spaced lines could be seen. This spectrum could be detected even after the solutions were stored at room temperature for a week; however, the visible absorption bands were found to fluctuate in intensity with time, and the solutions did not obey Beer's law. Quenching a day-old solution of 0.55 g. of II in 17.96 g. of sulfuric acid in ice-water resulted in recovery of 42% of starting material and 28% of a compound, whose m.p. (99.5-100.5°, reported(6) 102°), infrared spectrum, and elemental analysis indicated the monosulfoxide III. Compound III could be redissolved in sulfuric acid to give a solution with the same e.s.r. derivative spectrum and visible absorption maxima as obtained from II in sulfuric acid. When the disulfoxide of II(6) (bis-p-methylsulfonylbenzene) was dissolved in 96% sulfuric acid a broad seven line e.s.r. derivative pattern with a coupling constant identical to that of the cation-radical of II, was observed. These observations indicate a similarity between the reactions of II and its sulfoxides and thianthrene(7,8) and its sulfoxides.



III

Conclusive evidence for the presence of the dithiohydroquinone dimethylether cation-radical was obtained by electrochemical oxidation. Using a rotating platinum electrode in acetonitrile solution with tetra-N-propylammonium perchlorate as supporting electrolyte, II was found to undergo a 1 electron oxidation at + 0.861 v. (vs. an Ag-0.01 Molar $AgClO_4$ reference electrode) with a second wave appearing at +1.43 v. When electrochemical oxidation of II in acetonitrile was performed in

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(7) H. J. Shine and L. Piette, J. Am. Chem. Soc., 84, 4798 (1962).
(8) E. A. C. Lucken, J. Chem. Soc., 4963 (1962)

the e.s.r. cavity at the peak of the first wave, a blue solution with an e.s.r. derivative spectrum similar to that obtained from solutions of II in sulfuric acid was obtained. The spectrum of the electrochemically generated radical did not show extraneous lines which had prevented an unequivocal assignment of coupling constants for the radical in acid. The spectrum consisted of seven broad lines with relative intensities which are a good fit for electron interaction with six equivalent protons. The spacing of the lines suggest a coupling constant, a_{CH_3}, of 4.56 gauss in acetonitrile and 5.33 gauss in sulfuric acid for the cation-radical of II.(9)

Each of the seven lines was further split by interaction with an even number of protons (these may be the four ring protons) but the resolution was not good enough to measure the coupling constant or establish the nature of the further interaction with certainty.

Our inability to resolve the ring proton hyperfine structure may in part be due to the presence of two rotational isomers of the cation-radical of II which may result in different coupling constants for the ring protons in different environments. Several examples of such rotational isomers have been reported for other ion-radicals (10). The large (4.56 gauss) methyl proton coupling constant suggests that the spin density on sulfur is relatively large. Consequently, the spin density on proton-bearing ring sites can be expected to be relatively small; however, no relation between a_{SCH_3} and spin density on S has been established. The g-value was 2.0086 ± 0.0004, higher than the free electron value normally associated with radicals in π-systems made up exclusively of first row

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(9) Solvent effects of this magnitude are not unexpected. cf. V. Gendell, J. H. Freed, and G. K. Fraenkel; J. Chem. Phys., 37, 2832 (1962).

(10) E. W. Stone and A. H. Maki, J. Chem. Phys., 38, 1999 (1963); J. R. Bolton, A. Carrington and P. F. Todd, Mol. Phys., 6, 169 (1963); P. H. Reiger and G. K. Fraenkel, J. Chem. Phys., 37, 2811 (1962).

elements, also suggesting that sulfur interaction with the unpaired spin does occur.

Cyclic voltammetric study in acetonitrile showed both anodic and cathodic peaks centered around the d.c. half-wave potential of II. At low frequencies, the re-reduction was incomplete, suggesting a half-life for the cation-radical of ~5 secs. As the potential was cycled several times, new oxidation peaks appeared at + 0.75 v. and + 1.0 v. (vs. SCE). In 1,2-dimethoxyethane, the half-life of the cation-radical of II was only of the order of 0.1-0.5 secs.; however, new oxidation peaks did not appear even after numerous cycles. A possible interpretation of these results is that solvation by acetonitrile stabilizes the radical but also is involved in the formation of new electro-active species.

The long wavelength charge-transfer (C-T) absorption band maxima of π-electron donors is a measure of their relative first oxidation potential(11). The C-T maxima of I with tetracyanoethylene and p-chloranil are reported to be at 980 mμ and 870 mμ respectively(3). The corresponding maxima of II with these acceptors, in methylene chloride, occur at 675 mμ and 600 mμ. Similarly, the ionization potential of II, as measured by the electron impact method, (12) is 7.35 ± 0.05 volts, compared to the reported ionization potential of I, by the same method, of 6.5 volts(13).

We conclude that the sulfur analog of the Wurster's Blue cation-radical, the dithiohydroquinone dimethylether cation-radical, although capable of more than transitory existence, is formed with more difficulty, and is less stable than Würster Blue.

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(11) A. Zweig, J. Phys. Chem., 67, 506 (1963).

(12) We wish to thank A. Struck and his group, of these laboratories, for this measurement.

(13) G. Briegleb, Elecktronen-Donator-Acceptor-Komplexe, Springer-Verlag Berlin (1961) p. 183