Electrooxidation of Benzene

Sir:

Despite the scattered reports of half-wave potential ($E_{1/2}$) values for the electrooxidation of benzene in nonaqueous solvents,[1-3] this oxidation has not been examined in detail. The major difficulty has been the large background current from the concurrent electrolysis of the solvent-electrolyte system which seriously interferes with the delineation of defined current for benzene. We wish to report the observation of a well-defined current-potential (*i–E*) wave for this oxidation in the solvent acetonitrile containing tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) as the supporting electrolyte at Pt electrodes. The utilization of TBAHFP instead of the more commonly used tetraalkylammonium perchlorates,[4] coupled with working in a controlled atmosphere drybox (water and oxygen less than 1 ppm) with carefully purified acetonitrile[4] allowed us to investigate this electrooxidation mechanism in some detail by cyclic voltammetry and coulometry.

The cyclic *i–E* curve for the oxidation of benzene is shown in Figure 1a (peak 1). The E_p values are +2.4 V *vs.* sce at a Pt-foil electrode and +2.75 V *vs.* sce at a Pt-film electrode. (The difference in E_p values between these two kinds of electrodes is due to the ohmic resistance of Pt film, 19 ohms/cm^2.) The absence of a reverse reduction wave on reversing the scan direction is indicative of an EC mechanism in which the benzene cation radical is removed through a fast homogeneous chemical reaction (C) following the electron-transfer step (E). At more cathodic potentials between 0 and −0.9 V *vs.* sce, a double wave due to reduction (see peaks 2 and 3 in Figure 1a) and a wave due to oxidation (peak 4) were observed. The cyclic *i–E* patterns at these negative potentials were compared to those for proton reduction (*p*-toluenesulfonic acid) in the same medium (see Figure 1b). Electrooxidation of hydrogen gas in this medium also exhibited similar cyclic *i–E* peaks.[5] The similarity of these *i–E* curves as well as the analysis that an equivalent amount of protons is formed for each electron removed during macroscale electrolysis have supported the reduction waves as being due to protons. Biphenyl electrooxidation (peak 5) also produces protons as products (see Figure 1c). The biphenyl oxidation potential compares well with the theoretical and experimental data,[1,6] again with no background interferences (E_p values are +2.25 V *vs.* sce at a Pt-film electrode and +1.85 V *vs.* sce at a Pt-foil electrode).

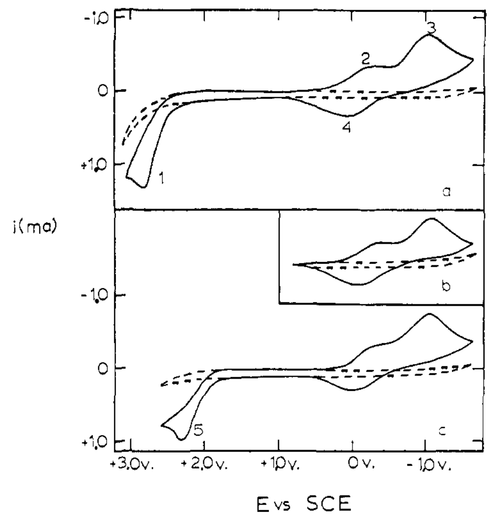

Figure 1. Cyclic *i–E* curves at a Pt-film electrode in 0.1 *M* tetra-*n*-butylammonium hexafluorophosphate–CH_3CN: a, oxidation of 1 m*M* benzene; b, reduction of 1 m*M* *p*-toluenesulfonic acid; c, oxidation of 1 m*M* biphenyl. Scan rate: 0.0404 V/sec; dotted line: background *i–E* curves in the same medium.

Stable benzene cation radicals have been generated successfully in a rigid sulfuric acid matrix using photolysis.[7] As was pointed out by Carrington, *et al.*,[8] hydrocarbon positive ions can lose ring protons if the medium in which the cation radicals are generated is sufficiently basic (in our case acetonitrile acts as a proton acceptor). Thus, the formation of protons from the electrooxidation of benzene and biphenyl confirms the conclusion of Carrington, *et al.*

Depending upon the initial benzene concentration and the rate of stirring, the observed benzene consumption during macroscale electrolysis was two to six times that predicted by the amount of charge passed. The final products were polymeric in nature. DMF dissolved some of this polymer and the resultant solution was highly fluorescent in the visible region of the spectrum. The fluorescence spectrum had characteristics of a mixture of polyphenylene compounds. This suggests that many isomeric polyphenylenes were formed with varying numbers of phenyl rings. The macroscale electrolysis products of biphenyl oxidation (dissolved in DMF) also showed a similar fluorescence response over the visible region.

The proposed mechanism for benzene oxidation is that the benzene cation radical forms, through loss of a proton, the phenyl radical. The phenyl radical now undergoes several reactions.[9] For example, it can undergo phenylation reactions or recombine with another phenyl radical to form biphenyl. Biphenyl is more easily oxidized at the oxidation potential of benzene producing the biphenyl cation radical. This cation loses a proton leaving a biphenyl neutral radical which can undergo further reactions such as those of phenyl radical.

It should be emphasized that each addition of a phenyl ring to any of the intermediates in the mechanism produces a polyphenyl compound which now can be more easily oxidized. Thus, as a result of this $(EC)_n$ reaction scheme, the polymerization proceeds until the higher molecular weight polyphenylenes precipitate.[10] This mechanism agrees well with that

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(1) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

(2) E. S. Pysch and W. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

(3) A. Yildiz, Ph.D. Thesis, University of North Carolina, 1968.

(4) T. Osa and T. Kuwana, submitted for publication. (TBAHFP was obtained from Ozark-Mahoning Co., Tulsa, Okla., and was recrystallized three times from 95% ethanol and dried in a vacuum oven at 60°).

(5) For typical electrochemical behavior of H^+/H_2 couple see S. Gilman, in "Electroanalytical Chemistry," A. J. Bard, Ed., Vol. 2, Marcel Dekker, Inc., New York, N. Y., 1967.

(6) L. Eberson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966).

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(8) A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

(9) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

(10) Attempts to identify biphenyl as one of the products (using gas chromatography) failed after most coulometric experiments. Only after drastic stirring conditions during the electrolysis were we able to

proposed for the cationic polymerization of benzene[11] (using metal ions as catalyst–oxidant).

The utility of electrochemically producing phenyl radicals for synthetic purposes and the similarities in the electrooxidation mechanisms of some larger fused aromatic hydrocarbons such as anthracene, naphthalene, and phenanthrene are under active investigation.

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detect some biphenyl. This absence of low molecular weight intermediates is indicative of an addition polymerization as proposed above (see F. W. Billmeyer, Jr., "Textbook of Polymer Chemistry," Interscience Publishers, Inc., New York, N. Y., 1957).

(11) P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).

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Azulene-Like Crystal Disorder in a Simple Thiepin. The Structures of Thieno[3,4-*d*]thiepin and Thieno[3,4-*d*]thiepin 6,6-Dioxide

Sir:

Recently, we reported the preparation of a remarkably stable simple thiepin system, thieno[3,4-*d*]thiepin (**1**).[1] The chemical and spectroscopic behavior of **1** has been compared to the thiepin sulfoxide **2** and the thiepin sulfone **3**.[2] These studies have shown that thiepin **1** possesses considerable aromatic-like character relative to heterocycles **2** and **3**.[2] It has been suggested that the unique properties of **1** may be due to ground-state contribution from azulene-like charge-separated species such as **4**.[1] In order to ascertain the nature of the π-electron delocalization in **1**, an X-ray determination of the molecular geometry of the thiepin along with the thiepin sulfone **3** was undertaken. We now wish to report that thiepin **1** is a planar system which has a crystal structure remarkably similar to the hydrocarbon azulene, while thiepin **3** shows nonplanar geometry which resembles that found for other thiepin sulfones.[3]

Thiepin **1** forms bright yellow plate-like crystals which are monoclinic, with $a = 8.273$, $b = 6.105$, and $c = 7.754$ Å, and $\beta = 103° 57'$. Systematic absences of the type ($h0l$) l odd, and ($0k0$) k odd, suggested the space group to be $P2_1/c$. However, the observed density (1.44 g/cc) indicated only two molecules per unit cell. Since the molecule lacks a center of symmetry, this implies that the structure is disordered with two molecules sharing four equivalent positions. Another possibility is that the true space group is Pc, the ($0k0$) absences being accidental; this would mean that there are two molecules per unit cell with no disorder.

Intensity data were taken at room temperature on a Picker 4-Circle automatic diffractometer with Cu Kα radiation, using the 2θ scan technique. Reflections (680) were recorded to a maximum 2θ angle of 130°, representing about 75% of the data theoretically accessible in the copper sphere. A sharpened three-dimensional Patterson function was calculated and heavy peaks corresponding to sulfur–sulfur vector interactions were observed. These could be explained equally well assuming an ordered structure (Pc) or a disordered structure ($P2_1/c$).

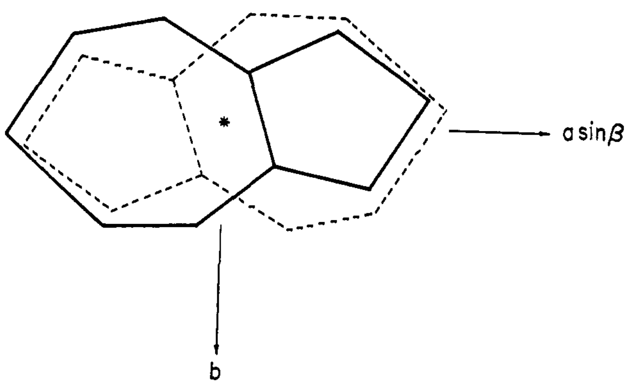

Figure 1. A projection of a portion of the disordered thieno[3,4-*d*]thiepin crystal structure viewed down the *c* axis. One molecule occupies either site randomly in the crystal lattice and this results in the center of symmetry shown by the asterisk. Disorder very similar to this occurs in the crystal structure of azulene.

Fourier syntheses phased on sulfur-scattering contributions were calculated for both space groups, and these were interpreted to give two trial model structures. Each model was then refined isotropically using least-squares refinement. The ordered structure refined isotropically to a residual of 16.2%; however, several large residual peaks were observed after difference Fourier synthesis. The disordered structure, on the other hand, rapidly refined to a residual of 12.8%, and no large peaks were observed after difference Fourier synthesis. Bond lengths and angles calculated at this time clearly favored the disordered structure to the ordered structure. This was confirmed by subsequent anisotropic least-squares refinement, which reduced the residual to 10.0% and gave acceptable bond lengths and angles.[4]

Figure 1 shows a portion of the structure as viewed down the *c* axis. The structure consists of thiepin molecules occupying the sites shown 50% of the time. Very similar disorder exists in the azulene crystal structure[5] whose unit cell constants and fractional atomic coordinates closely resemble this thiepin structure. Azulene, in addition, forms molecular complexes with trinitrobenzene[6] and Mo_2Co_6[7] which have similar disorder. Least-squares planes have been calculated for the thiepin ring and these show the molecule to be almost planar. The two sulfur atoms, however, deviate significantly from the molecular least-squares plane (0.06 Å) and this gives the molecule a slight boat shape. Similar but smaller deviations from planarity have been found in azulene.[8] Although the crystal disorder limits the accuracy of this analysis, the transannular carbon–car-

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(4) Refinement of this structure is continuing by full-matrix least-squares analysis. The complete details of the structure analysis of **1** will be published elsewhere.

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(8) Deviations of carbon atoms in analogous positions in azulene are 0.0088 Å. See ref 6.