

References and Notes

- (1) N. J. Maraschin, B. D. Catsikis, L. H. Davis, G. Jarvinen, and R. J. Lagow, *J. Am. Chem. Soc.*, **97**, 513 (1975).
- (2) A. J. Otsuka and R. J. Lagow, *J. Fluorine Chem.*, **4**, 371 (1974); R. J. Lagow and J. L. Margrave, *Polym. Lett.*, **12**, 177 (1974).
- (3) N. J. Maraschin and R. J. Lagow, *J. Am. Chem. Soc.*, **94**, 8601 (1972).
- (4) R. Eujen and R. J. Lagow, *Inorg. Chem.*, **14**, 3128 (1975).
- (5) E. S. Alexander, R. N. Haszeldine, M. J. Newlands, and A. E. Tipping, *J. Chem. Soc. A*, 2285 (1970).

Edmund K. S. Liu, Richard J. Lagow*

Department of Chemistry, University of Texas at Austin
Austin, Texas 78712

Received August 13, 1976

Anodic and Cathodic Reactions on a Chemically Modified Edge Surface of Graphite

Sir:

We have recently reported that carbon electrodes can be chemically modified to produce a chiral surface.¹ Thus, an electrode which had been heated in air was successively treated with thionyl chloride and (*S*)-phenylalanine methyl ester ((*S*)-PheM) producing a material labeled (*S*)-C_{ei}PheM. This was used as a cathode in aqueous solution to produce chiral alcohols from prochiral ketones, indicating that (*S*)-C_{ei}PheM was capable of inducing asymmetry. These experiments (with suitable controls) demonstrated the feasibility of achieving more selective electrochemical processes through chemical modification of electrode surfaces. A number of questions concerning the structure of C_{ei}PheM and the mechanism of electrode reactions on such surfaces were raised by this initial study. For example, since carbon electrodes are primarily composed of graphitic microcrystallites, and since graphite has two kinds of crystal faces, edge and basal,² it was of interest to know if modification and, therefore, asymmetric synthesis was taking place on one or both of these surfaces. This was tested using highly ordered pyrolytic graphite, and the results are reported here. A wide variety of applications were also suggested by the initial study. We report here that amino acid modified carbon electrodes can be used at positive potentials. This allowed us to perform the first asymmetric anodic reaction.

Highly ordered pyrolytic graphite (HOPG)³ has not to our knowledge been used for preparative electrochemistry. It is interesting to us because it has a structure closely similar to a single crystal of graphite. Therefore, each piece has well-defined edge surfaces and basal surfaces, and these can be used independently.⁴ A perfect basal surface is simply one layer of carbon atoms in the graphitic array. The edge surface is composed of the layer ends and is generally covered with surface oxides. Thus, it is expected that the chiral modifier will be attached at the edge surface via the surface oxides.¹

Two pieces (0.5 (edge height) × 2 × 3 cm) of HOPG were treated with SOCl₂ and (*S*)-PheM as usual.¹ The modified electrodes (HOPG-PheM) were then masked. On one piece, the edge surface was covered with silicon rubber so that electrochemistry could only occur on the basal surface. This electrode was used in 50% ethanol, 50% aqueous buffer acetate at -1.1 V vs. SCE for the reduction of 4-acetylpyridine (**1**)¹ and gave optically inactive **2** (yield >90%). The basal surface of the second piece was coated with silicon rubber. Reduction

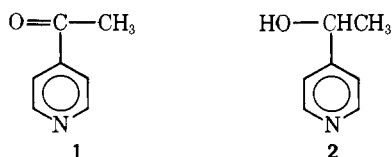


Table I. Photoelectron Spectroscopy Results^a

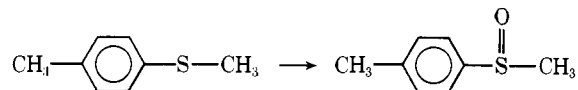
| Sample | Band intensity (Counts/s) | | | | |
|---------------------------------|---------------------------|-------|--------|-------|-------|
| | C(1s) | N(1s) | Cl(2s) | S(2p) | O(s) |
| HOPG + SOCl ₂ | 49K | Nil | 600 | Nil | 3.5K |
| HOPG + SOCl ₂ + PheM | 54K | 660 | 300 | Nil | 12.5K |
| HOPG + PheM | 50K | Nil | Nil | Nil | 5.0K |

^a Results from the edge surface of HOPG.

using the edge surface gave (-)-**2** (yield >90%) with enantiomeric excess of 2%. This result indicates that the asymmetric chemistry is taking place on edge surfaces, not basal, when a carbon rod is used.

This conclusion has been reinforced by x-ray photoelectron spectroscopy (XPS or ESCA). Four samples of HOPG were analyzed⁵ for N, S, Cl, and C. The first was an unmodified piece and little N, S, or Cl was found in either surface. The second was HOPG which had been treated with SOCl₂ and then washed with acetone. It showed a markedly increased Cl signal but no S signal (Table I). The third sample was treated successively with SOCl₂ and the PheM and washed as usual. It showed a strong nitrogen signal from the edge surface. The basal surface did show nitrogen, but only about 20% of that from the edge.⁶ A sample of HOPG which had been soaked in phenylalanine methyl ester solution and then thoroughly washed with water and acetone gave no nitrogen signal on the edge.

Finally, we wish to report that the anodic, asymmetric synthesis of sulfoxides⁶ is possible on C_{ei}PheM and that a similar differentiation of edge and basal chemistry is seen on modified HOPG. The reactant was *p*-tolyl methyl sulfide. As described in the accompanying communication the corresponding sulfoxide can be produced anodically in high chemical yield. On graphite in 2% aqueous acetonitrile at 1.1 V vs. Ag|0.1 M AgNO₃ in CH₃CN, it is formed in >90% current and material yield.



Using (*S*)-C_{ei}PheM under these same conditions the product sulfoxide (chemical and electrical yield >90%) is optically active (enantiomeric excess 2.5% of (-)). Optical purity was assured by an unchanged rotation after gas chromatographic purification. Oxidation on the basal surface of HOPG modified as above with (*S*)-phenylalanine methyl ester gave optically inactive sulfoxide. Oxidation on the edge surface of (*S*)-HOPG-PheM gave optically active product (enantiomeric excess 0.5% of (-)).⁸

Thus, the results in total demonstrate that HOPG is useful for preparative electrochemistry, that HOPG-PheM is modified on the edge surface, not basal, and the modification is useful at positive potentials. These data seem transferable to results on ordinary carbon and indicate that the activity of modified carbon electrodes results at least in part from electrochemistry on the edge surfaces of microcrystallites of graphite and not from modified basal surfaces.

Acknowledgment. This work was supported by the National Science Foundation.

References and Notes

- (1) B. F. Watkins, J. R. Behling, E. Kariv, and L. L. Miller, *J. Am. Chem. Soc.*, **97**, 3549 (1975).
- (2) J. S. Mattson and H. B. Mark, "Activated Carbon", Marcel Dekker, New York, N.Y., 1971.
- (3) Supplied by Dr. A. Moore, Union Carbide Corporation, Parma, Ohio.
- (4) I. Mocros and E. Yeager, *Electrochim. Acta*, **15**, 953 (1970).

- (5) The spectra were obtained on the DuPont instrument at the University of North Carolina. Results on silylated carbon electrodes are reported independently, C. M. Elliott and R. W. Murray, *Anal. Chem.*, in press.
- (6) The basal surface is not a perfect planar sheet. It is, therefore, possible to bind at dislocations as well as adsorb. This can account for the nitrogen signal.
- (7) B. Firth and L. L. Miller, *J. Am. Chem. Soc.*, following paper in this issue.
- (8) Optical yields are lower using the edge surface than the spectroscopic rods. The reason(s) for this is under investigation, but most likely involves differences in the surfaces.
- (9) Address correspondence to this author at the Department of Chemistry, University of Minnesota, Minneapolis, Minn. 55455.

Bruce E. Firth, Larry L. Miller*⁹
Michiharu Mitani, Thomas Rogers

Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

John Lennox, Royce W. Murray

Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Received July 7, 1976

Oxidations on DSA and Chirally Modified DSA and SnO₂ Electrodes

Sir:

The chemical modification of electrode surfaces has recently come under investigation in our laboratories. Our goal is to produce interfacial regions which can be used to perform specific and unique reactions. Initial approaches have concentrated on synthesizing chiral electrode surfaces by binding electroinactive, chiral compounds to conductors. Such chiral electrodes are then used to perform asymmetric electrode reactions. This approach was selected because asymmetric synthesis requires a chiral reagent. It, therefore, provides a sensitive probe for a successful modification which remains intact and "active" during use. The first reported example is the preparation of "(S)-C₆₁PheM" involving binding (S)-(-)-methyl phenylalanate to a carbon electrode via the surface oxides.^{1,2} This material was used to produce optically active alcohols by the reduction of ketones.¹

In the present study we have prepared chiral surfaces from DSA³ and SnO₂ electrodes and used them for preparative, asymmetric oxidations. Evidence is available which indicates that metal oxides can be chemically modified by silylation,^{4,5} but these materials have not been used for preparative electrolysis. It was hoped that "active" and stable surfaces could be prepared which would be useful for anodic synthesis.

To our knowledge DSA electrodes have not been previously used for preparative organic electrochemistry and we have, therefore, investigated the use of this material without surface modification. It is found that the onset of background in CH₃CN containing 4% H₂O is about 1.8 V vs. Ag|AgNO₃ in CH₃CN. The surface is quite stable in this solvent at 1.5 V, and very high current densities are supported. Several reactions, e.g., cyclization of laudanoline⁶ and conversion of 1-anisylethanol to *p*-methoxyacetophenone, proceed with yields equivalent to those obtained using platinum. Therefore, these electrodes seem to be a promising addition to the limited list of useful anodes.

Modification of antimony doped SnO₂ on a glass backing and DSA on a titanium backing was achieved by the following procedure. The electrode (general dimensions 30 × 80 mm) was placed in 100 ml of dry benzene (distilled from CaH) containing 3 ml of γ -aminopropyltriethoxysilane. The electrode was transferred after 30 min⁷ to a dry benzene solution of (-)-camphoric anhydride (2 g in 100 ml). After 24 h the electrode was removed, washed with acetone, and was ready for use.⁸ In the case of the DSA electrodes the titanium backing

Table I. Optical Purity of Sulfoxides^a

| Electrode | Reactant | Potential (V) ^b | Enantiomeric excess -2 (%) |
|---------------------------|-----------|----------------------------|----------------------------|
| Modified DSA | 1a | 1.4 | 0.9 ^c |
| | 1a | 1.1 | 0.8 |
| | 1b | 1.1 | 0.3 |
| Modified SnO ₂ | 1a | 1.8 | 1.4 |

^a Oxidations performed as described in text. ^b Measured vs. Ag-|AgNO₃. ^c Average of four runs. Deviation of $\alpha_{589} \pm 0.1^\circ$. $\alpha_{\text{obsd}} - 0.045$ (c 3, CHCl₃).

was covered with Dow Corning Silastic 732 RTV after functionalization.

There are to our knowledge no reports of asymmetric, anodic reactions. The anodic process chosen for study was the conversion of an aryl methyl sulfide to the sulfoxide. This reaction is relatively simple and proceeds in high chemical yield.⁹ The sulfoxide molecules are chiral and the production of optically enriched product constitutes the test of successful modification.

The oxidation was carried out in a three-compartment cell using Ag|0.1 M AgNO₃ in CH₃CN as a reference electrode. The electrolyte consisted of 15 g of tetraethylammonium fluoroborate in 140 ml of acetonitrile and 10 ml of water.⁹ In a typical experiment on DSA the potential was held at 1.4 V, background current was 20 mA, initial current from 500 mg of **1a** was 150 mA and after passage of 2 faraday/mol the final current was 30 mA. On SnO₂ at 1.8 V a typical background was 1 mA, initial current from 500 mg of **1a** was 28 mA and final current 2 mA. The products were isolated by evaporation of the anolyte, followed by addition of 100 ml of water and extraction with two 100-ml portions of ether. Rotary evaporation after drying the ether over anhydrous MgSO₄ gave the crude sulfoxide (~350 mg, current yield 65%) which was purified by chromatography on silica gel using CHCl₃ as eluent or by preparative TLC using a 1:1 mixture of chloroform and ethyl acetate as developer. All oxidations were run at room temperature under air (no change was observed if the reaction was run under argon or nitrogen) with the solution stirred with a magnetic stirrer.

The enantiomeric excesses shown in the table are of a low magnitude,¹⁰ but they are quite reproducible and further purification by chromatography gave sulfoxide with an unchanged rotation. Crystallization gave material with higher rotations as is common for such compounds.¹¹ Rotations were taken at four wavelengths. Partially resolved material was compared to the electrolysis product and direct proportionality between all readings was obtained. The optical purity of the product was established by NMR using tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III). The methyl signal of a partially resolved sample split into a doublet and allowed the specific rotation of pure **2a** to be assigned as $\alpha_{20,589}^{20} 167^\circ$. The rotation of optically pure **2b** is $\alpha_{20,589}^{20} 146^\circ$.¹² Although the selectivity is not useful for asymmetric synthesis, it is comparable to the results obtained in similar conversions using chiral chemical reagents.¹¹ We have made a specific comparison using **1a** with (+)-percamphoric acid¹³ which produced **2a** with enantiomeric excess +1.4.

To test the possibility that an adsorbed chiral reagent would be effective, a comparison experiment was conducted by oxidizing **1a** under the same conditions as above except that an unmodified DSA electrode was used and (+)-camphoric acid (equimolar with **1a**) was added to the anolyte. An electrode which had only been silanized was used in separate experiments with and without camphoric acid. In each case **2a** was isolated but was optically inactive. An attempt was also made to directly bind (+)-camphoric anhydride to DSA by soaking the