

Anodic Acetoxylation of Anisole at Graphite and Platinum Electrodes

C.Thillaiyadi Valliammai, M.Pugazhenthii and S.Sivaji Ganesan

Department of Chemistry, AVVM Sri Pushpam College (Autonomous), POONDI-613503 (TN) INDIA.

Abstract: Anodic acetoxylation of anisole has been carried out on graphite and platinum electrodes in glacial acetic acid and sodium acetate. On graphite electrode p-acetoxy anisole is the major product along with hydroxy derivative in traces. By using platinum electrode, the major product is dimer along with hydroxy derivative in traces. The most probable mechanism has been proposed.

Keywords: Anodic acetoxylation, Anisole, Graphite and platinum electrodes.

I. Introduction

Anodic acetoxylation of p. methyl anisole in glacial acetic acid using graphite and boron doped diamond have been studied by Fankhauser and his Co-workers¹. A number of other workers hold similar such views²⁻⁴. In the present work, anodic acetoxylation of anisole has been carried out on graphite and platinum electrodes in glacial acetic acid and sodium acetate.

II. Experimental

Materials

Anisole (BDH) was purified by vacuum distillation. The purity was checked by physical parameters and confirmed by TLC.

III. Electrochemical Process

The anodic acetoxylation reaction was carried out galvanostatically in a divided cell and locally fabricated 5v-100mA regulated DC power supply. The potentials were measured as cell voltages. Current voltage studies were performed with graphite and platinum anode in glacial acetic acid and sodium acetate.

The anolyte contained 0.1M substrate in 5% glacial acetic acid 20% sodium acetate mixture. Assuming 2electron process to occur depending on the intensity of current realized at the given potential, the duration of current passed was fixed whenever current decrease was unduly large either the polarity was reversed or potential was taken to zero volt for a short period as practiced in established electro synthetic works^{5,6}.

Product Analysis

The organic product mixture was separated by ether extraction and resolved on TLC test plate, using 10:1 benzene-ether mixture as eluent. The products were identified by means of co-TLC, physical constants, chemical analysis and pmr spectral analysis.

IV. Results And Discussion

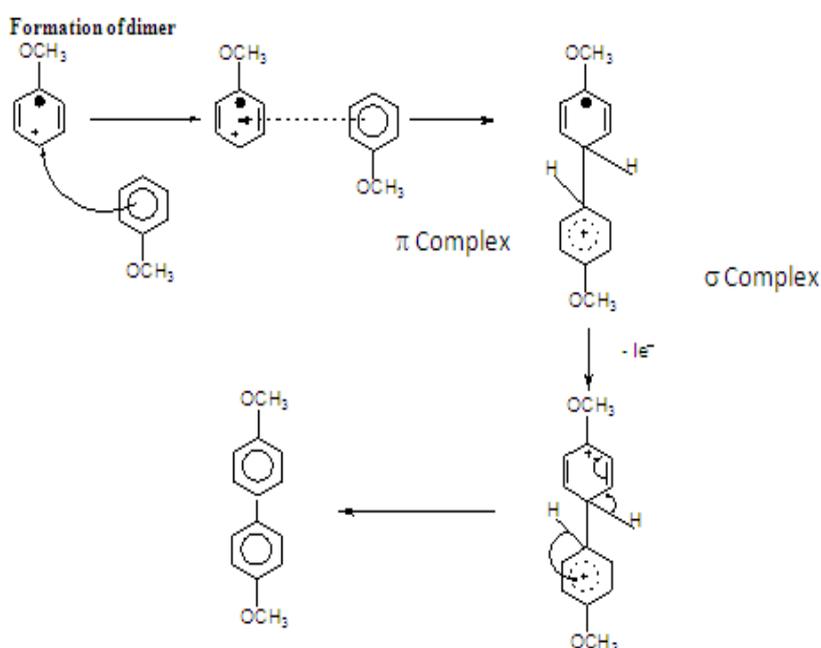
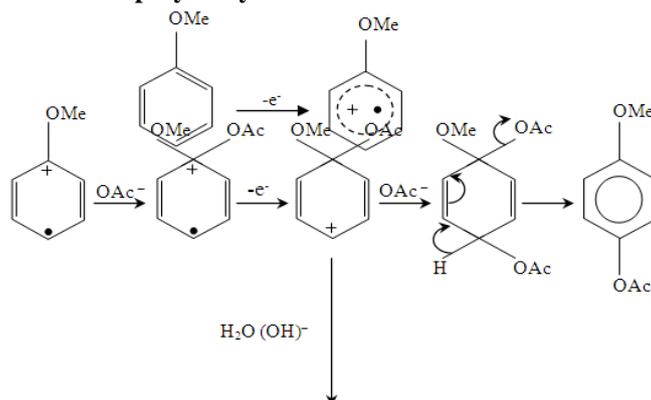
The current voltage curves for the systems suggests, the working potential range on graphite anode was observed to be 0.9 v to 1.0v. The working potential range on platinum anode was observed to be 1.4v to 1.85v. By using graphite electrode, p-acetoxy anisole as the major product and hydroxy anisole in traces. On platinum electrode, dimer as the major product along with hydroxy anisole in traces.

Graphite anode facilitates adsorption controlled phenomenon, on platinum anode diffusion controlled process occurs. By using graphite or platinum loss of 1 electron occur from the system initially to form radical cation.

On graphite anode, radical cation gets chemisorbed and it is induced by nucleophilic attack of OAC^- . This results in nucleophilic addition. By using platinum anode different situation arises. As soon as radical ion is formed it gets diffused into the bulk solution away from the electrical double layer. The labile radical ion undergo dimerisation and it might be exposed to nucleophilic attack by OAC^- in the solution.

The attack of the neutral substrate molecule with its π electron density on the cation radical to form π complex. The π complex thus formed may subsequently develop into σ complex which is again a radical ion. The σ complex further undergo second 1-electron transfer to form the dication. On deprotonation, dimers results.

The following mechanism has been proposed for acetoxylation of anisole
 Formation of p-acetoxy anisole and p-hydroxy anisole



Such a multiplex approach finds references in the earlier literature. 1,4-Dimethoxybenzene has been reported to undergo electrochemical reactions in three different pathways viz., ring substitution, *ipso* substitution and quinone formation⁷⁻¹⁰. On platinum the attack of the neutral substrate molecule on the cation radical to yield the dimerized product has been favorably proposed¹¹⁻¹².

References:

- [1]. Ulrich Griesbach, Andreas Fischer, Hermann Putter and Christos Comniellin, *J. Electroanal. Chem.*, 614 (2008) 107-112.
- [2]. Kowalski, J., Ploszynska, J., Sobkowiak, A., Moraycki, J. W., and Wilczewska, A. Z., *J. Electroanal. Chem.*, 4 (2005) 275-280.
- [3]. Toshio Fuchigami, Yuki Nakagawa and Tsutomu Nonaka *Tetrahedron* 27 (1986) 3869-3872.
- [4]. J. Hoffmann and A. Sarafidis, *Jovoss, Electrochimica Acta*; 36 (1991) 1165-1169.
- [5]. H. J. Schafer *Topics in Current Chemistry*; 152 (1990) 91.
- [6]. Lines Robert and H. P. Utley James, *J. Chem. Soc. Perkin Trans. II* 803 (1977).
- [7]. J. Wang, M. Jiang, and F. Lu, *J. Electroanal. Chem.* 444 (1998) 127.
- [8]. C. X. Zhao, Y. F. Gong, H. Y. He and X. K. Jiang, *J. Phys. Org. Chem.*, 12, 688 (1999)
- [9]. J. H. Dong, H. Y. Dou and C. X. Zhao, *J. Fluorine Chem.*, 127, 205 (2006)
- [10]. Fischer, A.; Show, Y.; and Swain, G. M., *Anal. Chem.*, 76 (2004) 2553
- [11]. Swain, G. M. In *Electroanalytical Chemistry*; Bard A. J., Rubinstein I. Ed., Marcel Dekker: New York, Vol. 22, (2003) 181
- [12]. Hasegawa, M.; and Fuchigami, T., *Electrochim. Acta* 2004, 49, 3367.