

SIDE-CHAIN ANODIC OXIDATION. MECHANISM OF BENZYL CATION FORMATION.

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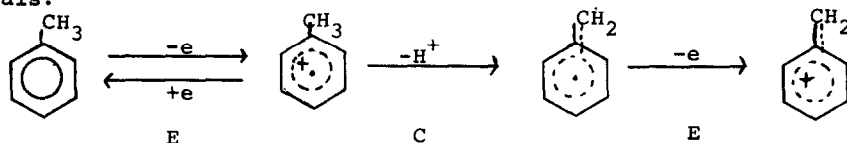
We would like to report the first concrete mechanistic evidence for side-chain oxidation of alkylaromatic compounds. The oxidation is an ECE process as shown by quantitative electrochemical techniques.

Side-chain acetoxylation has been proposed to involve formation of benzyl cation by direct two electron (2-e) transfer followed by proton ejection (1). The 2-e oxidation has been advocated also for side-chain acetamidation of hexamethylbenzene (2,3). The latter mechanism has been criticized on the basis that bibenzyls, which could only arise from benzyl radicals, are major products in some cases (4). Benzyl radicals also have been implicated as precursors of side-chain acetoxylation products since both side-chain methylation (which no doubt occurs by combination of methyl and benzyl radicals) and side-chain acetoxylation of mesitylene are completely suppressed with graphite anodes (nuclear acetate yields are comparable to those obtained at platinum (5)).

The anodic cyclic polarogram of pentamethyl anisole is shown in Figure 1,A (6). Two oxidation peaks are observed on the first scan and on reversal, a current is seen corresponding to reduction of the intermediate formed at the first oxidation peak. The cathodic peak at about 0 v. vs SCE is due to reduction of protons formed in the oxidation. Figure 1,B shows the effect of added water (0.6M), the second oxidation peak is shifted cathodic and the first peak can barely be seen as a discrete peak. The first oxidation peak involves 1-e as proven by comparison of the peak height with that obtained from equimolar

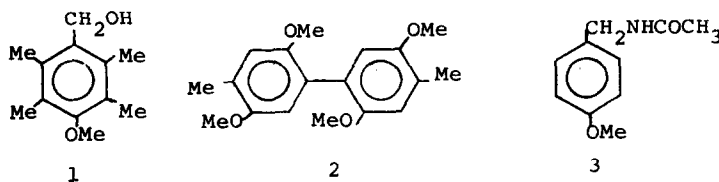
1,4-dimethoxybenzene. The latter gives a well established 1-e peak (7). The fact that 1-e is transferred and a proton is formed at the first peak indicates the cation-radical is the initial product and undergoes a proton ejection follow-up reaction.

We propose the following mechanism for anodic side-chain oxidation. The first step is a 1-e oxidation to cation-radical. An irreversible proton loss occurs forming benzyl radical which is oxidized at slightly more anodic potentials:



2,5-dimethoxytoluene exhibits similar voltametric behavior (Figure 1,C). Two anodic peaks are observed, and if the potential is switched after the second peak, reduction current is observed corresponding to the reduction of the intermediate formed at the second oxidation peak. If the scan is reversed between the two oxidation peaks, reduction current is observed for the first oxidation peak and the proton wave is still observed. The cation-radical is the initial product and undergoes a follow-up reaction involving the ejection of a proton. With p-methoxytoluene the first oxidation peak corresponds to the transfer of two electrons and a proton peak is observed (Figure 1,D).

Preparative electrolysis in acetonitrile-water (0.6 M)-tetraethylammonium perchlorate (0.1 M), shows a different reaction is involved in the three cases. The product structures, 1-3, were determined by IR and NMR after isolation by glc. In each case, only one product was observed by glc.



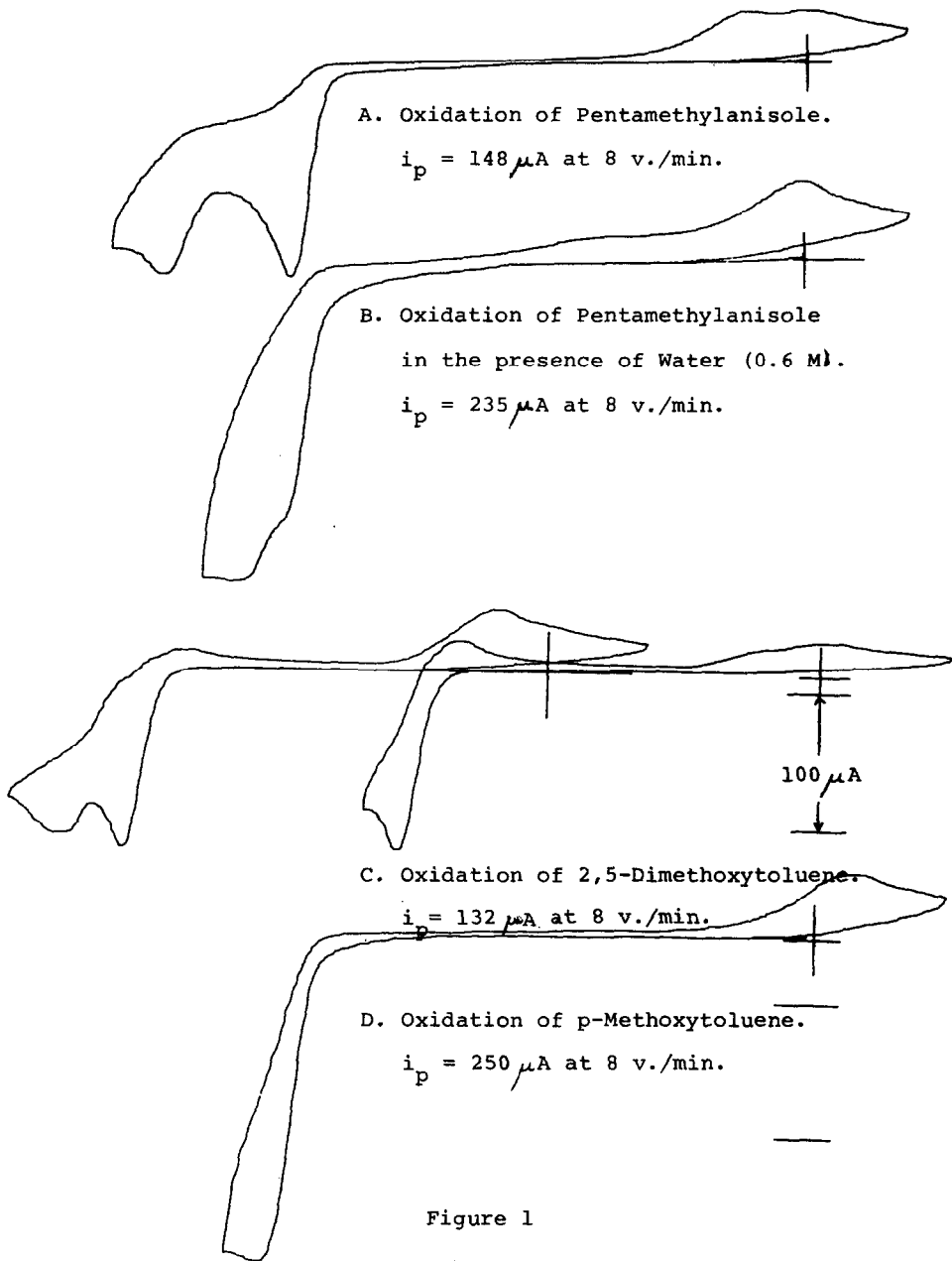


Figure 1

The differences in behavior of p-methoxytoluene and the more substituted compounds is explained as follows. The corresponding cation-radicals, radicals and cations of the three compounds have varying stabilities. Pentamethylanisole produces a relatively stable cation-radical. Loss of a proton and further oxidation produces a relatively stable cation (stability refers to the time scale of cyclic voltammetry). 2,5-dimethoxytoluene produces a relatively stable cation-radical which prefers to dimerize rather than eject a proton. p-Methoxytoluene gives a cation-radical which ejects a proton and is further oxidized. Solvent (acetonitrile) interaction follows. The rapid consecutive steps are not separated by the techniques used; thus two electrons appear lost in one step. p-Methoxytoluene undergoes side-chain acetamidation in large scale electrolysis in acetonitrile (0.6 M water). The pentamethylanisole cation reacts with water rather than acetonitrile. The cations from alkylaromatic compounds that show one electron oxidation in acetonitrile are selective (do not react with the solvent) and those from compounds that undergo two electron oxidation are non-selective. Non-selective cations acetamidate in acetonitrile even with relatively high concentrations of water, a much better nucleophile.

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