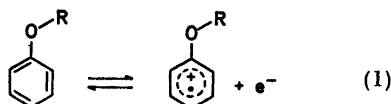


# The Relative Ease of Oxidation of Phenols and Phenolic Ethers. A Comparison of Reversible Redox Potentials

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The oxidation processes of phenols are of great interest in both organic and biological chemistry.<sup>1</sup> It is a common observation that phenols are more easily oxidized than the corresponding ethers. The latter is not what one would predict by comparing the ability of an alkyl group with a hydrogen atom to inductively supply electrons to the phenoxy moiety. Here we report reversible redox potentials of some simple phenols and their corresponding methyl ethers and present conclusive evidence that  $E^\circ$  for reaction (1) is in general more positive for a phenol ( $R=H$ ) than for the ether ( $R=Me$ ). The only reversible redox potentials previously



reported for phenolic compounds involved special structural features, the  $\alpha$ -tocopherol model compound<sup>2</sup> and bridged biphenyls.<sup>3</sup>

Voltammetric data for several phenols and the corresponding methyl ethers are summarized

in Table 1. In dichloromethane at  $-50^\circ\text{C}$  all of the phenols gave irreversible oxidation peaks while two of the ethers, 1,4-dimethoxybenzene and 4-methoxybiphenyl gave reversible cyclic voltammograms. The first column in the table summarizes peak potentials in dichloromethane at  $-50^\circ\text{C}$ . The second column shows data from the same solutions after adding  $\text{HFSO}_3$  (10 %).<sup>4</sup> The fact that the peak potentials for the two ethers showing reversible behaviour did not change upon addition of the acid indicates that the changes in peak potentials for the phenols given in the third column are the differences between the irreversible and reversible oxidation potentials and do not arise from changes in the solvent or in the reference electrode. The data are exemplified by the cyclic voltammograms of 4-hydroxybiphenyl in dichloromethane ( $\text{Bu}_4\text{NBF}_4=0.2\text{ M}$ ) shown in Fig. 1. In the absence of acid (Fig. 1a) a single irreversible oxidation peak was observed at  $+1.48\text{ V}$ .<sup>5</sup> In

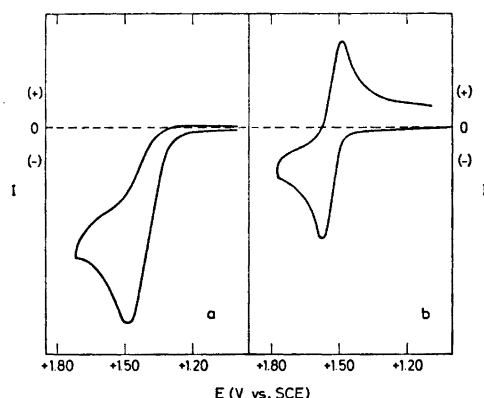


Fig. 1. Cyclic voltammetry at a platinum button electrode of 4-hydroxybiphenyl ( $2 \times 10^{-3}\text{ M}$ ) in dichloromethane ( $\text{Bu}_4\text{NBF}_4=0.2\text{ M}$ ) at  $-50^\circ\text{C}$  and  $86\text{ mV/s}$ . (a) in the absence of acid, (b) in the presence of  $\text{FSO}_3\text{H}$  (10 %).

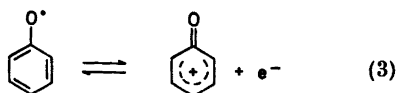
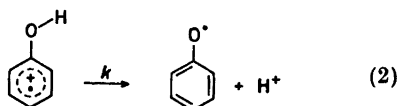
Table 1. Reversible oxidation potentials of phenols and phenol ethers.

Compound	$E_p^{\text{ox}}$ (V vs. SCE)		Shift (mV) <sup>c</sup>	$k$ ( $\text{s}^{-1}$ ) <sup>d</sup>
	$\text{CH}_2\text{Cl}_2$ <sup>a</sup>	$\text{CH}_2\text{Cl}_2\text{-HFSO}_3$ <sup>b</sup>		
4-Methoxyphenol	1.20	1.49	290	$2.1 \times 10^{10}$
1,4-Dimethoxybenzene	1.38	1.39		
4-Hydroxybiphenyl	1.48	1.59	110	$1.8 \times 10^4$
4-Methoxybiphenyl	1.55	1.56		
2,4,6-Trimethylphenol	1.33	1.65	320	$2.2 \times 10^{11}$
1-Methoxy-2,4,6-trimethylbenzene	1.70	1.68		

<sup>a</sup>  $[\text{Bu}_4\text{NBF}_4]=0.2\text{ M}$ ,  $-50^\circ\text{C}$ , voltage sweep rate= $86\text{ mV/s}$ . <sup>b</sup> Acid concentration=10 % by volume. <sup>c</sup> Differences in reversible and irreversible peak potentials. <sup>d</sup> Estimated first order rate constants for deprotonation of the cation radicals at  $-50^\circ\text{C}$ .

the presence of  $\text{HFSO}_3$  (10 %) the voltammogram (Fig. 1b) showed that the cation radical was stable during the time scale of the experiment. Further addition of acid had no effect upon the reversible potential (+1.59 V) indicating that kinetic processes were no longer operative and that the value approximates  $E^\circ$ .

In the cases studied, the irreversible potentials measured in the absence of acid were always considerably lower for the phenols than for the ethers while those measured from reversible voltammograms, except for 2,4,6-trimethylphenol, showed the opposite order, i.e. the phenol potentials were more positive than those of the ethers. Differences in voltammetric peak potentials measured under reversible and irreversible conditions are due to the occurrence of chemical reactions coupled to the electron transfers.<sup>6</sup> The source of the large differences between the irreversible and reversible potentials for the phenol oxidations is no doubt connected to the deprotonation of the cation radical (2) accompanied by the generation of the phenoxy radical which is more easily oxidized than the phenol. Further electron transfer then occurs generating the phenoxonium ion (3), a species very susceptible to attack by any nucleophiles present in the medium.<sup>1</sup> From the differences in the potentials between the reversible and irreversible voltammograms, the rate constants for steps (2) can be calculated by the method of Nicholson and



Shain.<sup>6</sup> Estimates of the rate constants for the deprotonation of the cation radicals are given in the last column of the table.<sup>7</sup>

It is of interest to note that the reversible potential for 2,4,6-trimethylphenol was less positive than that of the corresponding ether. A similar effect has been observed during a comparison of ionization potentials of phenols and phenol ethers.<sup>8</sup> The gas phase ionization potential of 2,6-dimethylphenol was found to be 0.25 eV less than 2,6-dimethylanisole while several other methyl phenols were found to have ionization potentials about 0.2 eV higher than the corresponding ethers. The reason for the increased difficulty of oxidation of 2,6-dimethylanisoles is apparently due to the fact

that the ether methyl group is hindered from occupying a position in the same plane as the aromatic ring and thus conjugation of the oxygen lone pair of electrons is diminished in the cation radical. It has previously been shown that such conjugation inhibition gives rise to unusual reactivity of phenol ether cation radicals.<sup>9</sup>

The results presented here are the first for the reversible oxidation of simple phenols. These, along with data from the corresponding ethers and gas phase ionization potentials<sup>8</sup> allow us to draw the conclusion that the  $E^\circ$  values for phenols in general are more positive than those for the ethers.

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4. The use of this solvent system for obtaining reversible potentials for aromatic hydrocarbons has previously been described, see: Hammerich, O. and Parker, V. D. *J. Amer. Chem. Soc.* 96 (1974) 4289.
5. All potentials refer to the saturated aqueous calomel electrode. Measurements were made vs. an  $\text{Ag}/\text{Ag}^+$  electrode in acetonitrile.
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7. The calculations for kinetic potential shifts<sup>6</sup> were made for the EC mechanism. Results of digital simulation calculations show that very nearly the same potential shifts should be observed for the ECE mechanism.
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