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Polarographic Investigations on Formylguaiacols and Veratrols

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The reactivity of guaiacols and veratrols is a problem of both theoretical and practical interest which has been extensively studied. In the present investigation the reactivity of various sites in the aromatic nucleus in these compounds has been studied using polarographic half-wave potentials of formyl derivatives.

Experimental. The polarographic experiments using a dropping mercury electrode were performed in the usual manner¹ at $25 \pm 0.1^\circ\text{C}$ with a Cambridge General Purpose polarograph equipped with an electronic recorder. The exact potentials were read from a Radiometer PHM 4 pH-meter and the resistances of the solutions from a Philips PR 9500/01 conductometer. The height of the mercury column was 58.5 cm, the drop weight $2.537 \text{ mg}\cdot\text{s}^{-1}$ and the dropping time in 0.1 N KCl 3.50 s. A saturated calomel electrode (SCE) was used as a reference electrode and the measurements were made in 0.1 N NH_4Cl - 40 % ethanol-water mixtures. No maximum suppressor was used. The accuracy obtained was $\pm 0.01 \text{ V}$.

The aldehydes investigated were of commercial origin. They were purified before use by sublimation *in vacuo*, distillation and recrystallisation. Ethanol of spectrograde quality (AaS) from Oy Alkoholiliiike Ab, Helsinki, showed no wave in the region investigated and was used as such.

Results. The results of the polarographic measurements are collected in Table 1.

Preliminary investigations on the dependence of halfwave potential and current on pH, concentration, and solvent, and the slope of the polarographic wave indicated that the present compounds follow generally accepted patterns for the reduction of aromatic monosubstituted aldehydes, *cf. e.g.* Ref. 2.

It has previously been found for guaiacylic as well as for other polysubstituted aromatic compounds in connection with

Table 1. Polarographic half-wave potentials (SCE) $E_{1/2}$ of aromatic aldehydes at 25°C in 0.1 N NH_4Cl -40 % ethanol-water mixtures. Concentration of aldehyde: 0.001 M.

No.	Substance	$-E_{1/2} \text{ V}$	$\Delta E_{1/2} \text{ V}$
1	Benzaldehyde	1.32	reference
2	Formylphenol	1.38	-0.06
3		1.31	+0.01
4		1.47	-0.15
5	Formylanisol	1.27	+0.05
6		1.41	-0.09
7	Formylguaiacol	1.31	+0.01
8		1.40	-0.08
9		1.41	-0.09
10	Formylveratrol	1.23	+0.09
11		1.38	-0.06

pK-determinations that every substituent alters the free energy of activation by a characteristic amount.³ A similar, roughly linear free-energy relation seems also to be valid in the present case. This could also be expected from the notable success in application of the modified Hammett equation in discussing polar substituent effects in the polarography of aromatic compounds:⁴

$$\Delta E_{1/2} = \rho\pi\sigma \quad (1)$$

$\Delta E_{1/2}$ denotes the shift in half-wave potential caused by a certain substituent, σ the total polar substituent constant and $\rho\pi$ expresses the susceptibility of the reduction process to the polar influence of substituents.

The correlation between the present polarographic data and other chemical evidence is clearly indicated by the plot in Fig. 1. There the polarographic half-wave potentials of the aldehydes in Table 1 are plotted against the rate data of Sarka-

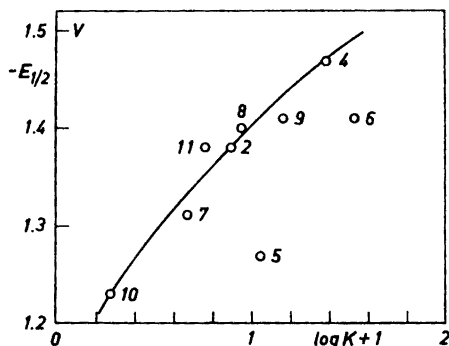


Fig. 1. Plot of half-wave potentials $E_{1/2}$ for aromatic aldehydes against rate of proto-deuteration in 57% HClO_4 of corresponding compound with the formyl group replaced by deuterium. The numbers refer to the list of compounds in Table 1.

nen *et al.*⁵ for the exchange of deuterium in corresponding deutero-phenols and anisols in 57% HClO_4 -solution. Thus we can verify from our data the same order of reactivity for electrophilic aromatic

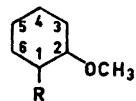


Fig. 2. R = OH, OCH_3

substitution as reported recently by the mentioned authors:⁵ guaiacol, $k_4 > k_5 > k_6$; veratrol, $k_4 = k_5 > k_3 = k_6$. The subindices refer to the positions in Fig. 2.

The order above is explicable in usual terms of inductive and mesomeric effects of the substituents⁶ and has been obtained by us also by LCAO-MO-calculations on the mentioned compounds. The investigations are continued.

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