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## A POLAROGRAPHIC STUDY OF THE OXIDATION OF SOME POLYHYDROXYBENZENES WITH ATMOSPHERIC OXYGEN

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### Preliminary communication

As a contribution to the study of the formation of humic acids in soil, a polarographic investigation has been made of the oxidation of some poly-hydroxybenzenes in aqueous solution under different conditions. The formation of hydroxyquinone as an intermediate in the oxidation of hydroquinone was confirmed. Indications were obtained for the identity of some other intermediate reaction products. The important conclusion is drawn that the presence of tyrosinase or certain clay-minerals frequently not only influences the reaction velocity, as is sometimes supposed, but also may alter the course of the oxidation reaction.

### Introduction

It is definitely established that the dark-brown colored, higher molecular organic acids in the soil, the so-called "humic acids", contain phenolic or quinonoid ringsystems. These acids, however, show a rather complicated structure (presumably heteropoly-condensates). To get a better insight into the processes which lead to the formation of humic acids in soils, in recent years much study has been devoted to the oxidation of di- and tri-hydroxybenzenes and their derivatives. In alkaline medium these substances react spontaneously with atmospheric oxygen, whereby similar dark-brown acids are formed. The oxidation can also be carried out enzymatically in neutral or weakly acidic solution. Some metal salts and also silicagel appeared to act as catalysts. For a review see *Scheffer* and *Ulrich*<sup>1</sup>.

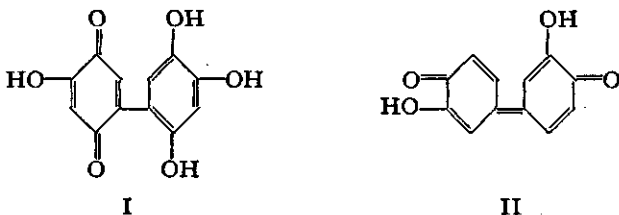
As regards the mechanism of these oxidation reactions under different conditions and with different phenolic substances, so far there are more (often contradictory) hypotheses than established facts. We have tried to elucidate these reactions by studying their course polarographically.

<sup>1</sup> *F. Scheffer* and *B. Ulrich*, *Lehrbuch der Agrikulturchemie und Bodenkunde* III. Teil, Humus und Humusdüngung, F. E. Verlag, Stuttgart 1960.

## 1. Hydroquinone

A comparative investigation was made of the oxidation of hydroquinone, quinone, quinhydrone and hydroxyquinone at different pH-values.

In accordance with the findings of *James, Snell* and *Weissberger*<sup>2</sup> and those of *Flaig* and *Salfeld*<sup>3</sup> hydroquinone in aqueous, weakly alkaline solution appeared to be oxidized primarily to *p*-benzoquinone and hydrogen peroxide, from which reaction products hydroxyquinone is formed. A wave with an  $E_{1/2}$ -value of about  $-0.85$  V is partially ascribed to dimers and possibly other simple polymers of hydroxyquinone, e.g. I. (See<sup>3</sup>). As expected, the presence of tyrosinase had no effect on the oxidation mechanism, nor could a catalytic affect of kaolinite or bentonite be detected.



## 2. Catechol

The first oxidation product in weakly alkaline solution also again appeared to be hydrogen peroxide, but no wave could be observed originating from *o*-quinone or 1,2,4-trihydroxybenzene, and only a faint wave of hydroxyquinone was observed. So there is a clear difference from the mechanism of the enzymatic oxidation of catechol at pH 6-7 as proposed by *Wagreich* and *Nelson*<sup>4</sup> or *Doskočil*<sup>5</sup>. A characteristic wave occurred with an  $E_{1/2}$ -value varying from about  $-0.45$  V at pH 8 to  $-0.60$  V at pH 9.5. The polarographic behaviour of the substance (A) causing this wave closely resembled that from 2,5-dihydroxyquinone, except that A was not stable in alkaline solution. For an assumed 2-electron reduction the maximum uptake of protons was 4. Possibly this substance is a partially oxidized dimer of catechol e.g. II. (See *Forsyth*<sup>6</sup>). At last an also transitory wave

<sup>2</sup> T. H. James, J. M. Snell and A. Weissberger, J. Am. Chem. Soc. 60, 98, 2048 (1938).

<sup>3</sup> W. Flaig and J. Chr. Salfeld, Paper read at the Congress Intern. Soil Sci. Soc. at Wisconsin, 1960.

<sup>4</sup> H. Wagreich and J. M. Nelson, J. Am. Chem. Soc. 60, 1545 (1938).

<sup>5</sup> J. Doskočil, Coll. Czech. Chem. Comm. 15, 599, 780 (1950).

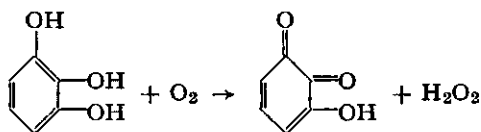
<sup>6</sup> W. G. C. Forsyth and V. C. Quesnel, Biochim. et Biophys. Acta 25, 155 (1957).

was observed with an  $E_{\frac{1}{2}}$ -value of about  $-0.85$  V (just as with hydroquinone) which is the sole occurring wave at lower pH (e.g. at pH 6.5).

In presence of tyrosinase, however, at pH 6.5, only a wave with  $E_{\frac{1}{2}}$  of  $-0.14$  V was observed; the reaction-velocity was much greater in this case. Kaolinite seemed only to decrease the oxidation-velocity (pH 7.5). Bentonite, however, strongly catalyzed the formation of substance A with  $E_{\frac{1}{2}}$  of  $-0.40$  V (in absence of bentonite at pH 7.5 this wave was not clearly distinguishable).

### 3. Pyrogallol

In weakly alkaline solution characteristic waves were observed with half-wave potentials of  $-0.48$  V and  $-0.84$  V, respectively. For an assumed 2-electron-reduction the maximum uptake of protons was 3. The first oxidation-step is therefore assumed to be:



This is in accordance with what is stated by *Flaig*<sup>7</sup>. The first-mentioned wave rapidly disappeared, but the wave with an  $E_{\frac{1}{2}}$  of  $-0.84$  V (for the greater part due to hydrogen peroxide) increased strongly for some time indicating that hydrogen peroxide is also formed during further oxidation-steps. No other characteristic waves were found, only a gradually rising curve which indicates the presence of a mixture of reducible products with only small differences in half-wave potentials.

At pH 6.4, firstly a wave was observed with an  $E_{\frac{1}{2}}$  of  $-0.85$  V in presence as well as in absence of tyrosinase. After one day, however, with tyrosinase this wave was substituted by three lower, faint waves with half-wave potentials of  $-0.7$ ,  $-0.1$  and  $-1.3$  V, respectively.

Kaolinite appeared to have no perceptible effect on the oxidation of pyrogallol. With bentonite, however, at the start a strong wave was observed with an  $E_{\frac{1}{2}}$  of about  $-0.47$  V, and some less pronounced ones at  $-0.65$ ,  $-0.85$  and  $-1.10$  V respectively. After a half day the polarogram showed a somewhat irregular wave with a considerably less negative  $E_{\frac{1}{2}}$ -value than in absence of bentonite. After two days the difference had nearly disappeared.

<sup>7</sup> W. Flaig, Sci. Proc. Royal Dublin Soc. A1, 149 (1960).

**Experimental details**

Use was made of the Blomgren Polarolyzer Type LKB 3266 with dropping Hg-electrode and a saturated calomel electrode as a reference electrode. The concentration of the phenolic substances investigated was 0.01 or 0.02% (supporting electrolyte  $M/10$   $KNO_3$  in 0.005% C.M.C.-solution). The buffer used was that of *Britton-Robinson*, containing  $H_3PO_4$ ,  $AcOH$  and  $H_3BO_3$ , the desired pH being adjusted with  $NaOH$ . Where used, tyrosinase was added in an amount of 2 mg/100 ml and bentonite or kaolinite in amounts of 100 mg/100 ml. The cell was kept at  $20^\circ$  by means of a thermostat. The drop-time was 3.5 sec. Oxygen was added by bubbling air through the cell or exposing the reaction mixture to the air for some time. Before measurements were made, gaseous and dissolved oxygen was removed from the solution by bubbling nitrogen through and over the solution. The half-wave potentials were determined graphically. No corrections were made for resistance and residual current.

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