

surface the adsorbed film is compressed to a rapidly dissolving scum, which provides the local centres of concentrated solution. This explanation is supported by the further observation that when the sweeping is made more sudden and drastic so as to remove all the upper part of the liquid from the vessel altogether, 'pockeling' appears to be absent. We have been able to see with the naked eye the crumpling of the adsorbed film on the surface of the solution of phenyl propionic acid. It is also supported by the fact that a moving bubble may carry along with it very many times the amount of solute which could find place in a monomolecular film or which would conform with the theorem of Gibbs.

The movement of the talc is made much more visible by providing a black background. This is very simply accomplished by coating the trough with black paraffin—a mixture of carbon black and ordinary paraffin. When the paraffin is in place, the surface is fused by passing a flame over it, causing the carbon particles to sink below the surface, thus preventing contact between the carbon particles and the solution.

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¹ Agnes A. Pockels, *Naturwiss.*, 9, 137, 149 (1917).

Abnormal Strength of 2:6-Dihydroxybenzoic Acids

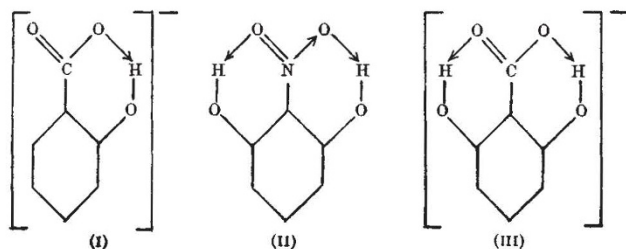
THE work of W. Ostwald¹ showed that the electrolytic dissociation constants of the hydroxybenzoic acids vary greatly with the positions of the hydroxyl groups. Thus the dissociation constants of benzoic acid, and of those mono-, di- and tri-hydroxybenzoic acids, which do not possess a hydroxyl group in the ortho-position to the carboxyl group, have dissociation constants all less than 1×10^{-4} ; the dissociation constants of the various hydroxybenzoic acids containing an ortho-hydroxyl group are all of the order of 1×10^{-3} , and 2:6-dihydroxybenzoic acid has a dissociation constant of 5.0×10^{-2} (see Table 1).

Dissociation Constants at 25°.²

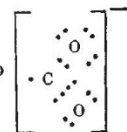
| | | | |
|-------------------------------|----------------------|---------------------------|-----------------------|
| Benzoic acid | 6.6×10^{-5} | Salicylic acid | 1.06×10^{-3} |
| <i>m</i> -Hydroxybenzoic acid | 8.3×10^{-5} | 2:3-Dihydroxybenzoic acid | 1.14×10^{-3} |
| <i>p</i> -Hydroxybenzoic acid | 2.9×10^{-5} | 2:4- " " | 0.52×10^{-3} |
| 3:4-Di " " | 3.3×10^{-5} | 2:5- " " | 1.08×10^{-3} |
| 3:5-Di " " | 9.1×10^{-5} | 2:3:4-Tri " " | 0.55×10^{-3} |
| 3:4:5-Tri " " | 3.8×10^{-5} | 2:6-Dihydroxy " " | 5.0×10^{-2} |

It will be seen that the constant for 2:6-dihydroxybenzoic acid is some fifty times greater than that of salicylic acid, and almost eight hundred times greater than that of benzoic acid. The acid is, indeed, stronger than either phosphoric or sulphurous acids.

The increased acidity of the salicylic acid derivatives over the other hydroxybenzoic acids is probably due to chelation of the anion³ (I), which would hinder the return of the proton and thus increase the degree of ionisation.

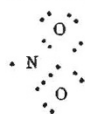


Now the ionised carboxyl group



bears

a strong formal resemblance to the nitro-group



, and it has been shown that a nitro-group

can chelate with *two* ortho-hydroxyl groups, since 2-nitroresorcinol (II) behaves as a fully chelated compound³. It therefore seems reasonable to suggest that an ionised carboxyl group also can chelate with *two* ortho-hydroxyl groups, and to represent the anion of 2:6-dihydroxybenzoic acid by the structure (III), in which state neither oxygen atom would readily accept a proton. No attempt has been made in (III) to indicate a resonance formula.

W. Madelung⁴ has proposed, on theoretical grounds, a formula closely resembling (III) for the anion of 2:6-dihydroxybenzoic acid, but the analogy of the anion with 2-nitroresorcinol affords strong experimental evidence in favour of the formula now advanced. The same type of structure must be assigned to the anions of other 2:6-dihydroxybenzoic acids; for example, phloroglucinol carboxylic acid ($k = 2.1 \times 10^{-2}$), and paraorsellinic acid ($k = 4.1 \times 10^{-2}$).

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¹ *Z. phys. Chem.*, 3, 241 (1899).

² Values taken from "Landolt Börnstein", *Physikalisch-Chemische Tabellen*, vol. 2 (1923).

³ W. Baker, *J. Chem. Soc.*, 1687 (1934).

⁴ *Ann. Chem.*, 427, 87 (1922).

South and East African Stone Age Typology

IN his recent letter¹, Prof. Dreyer remarks that discoveries in East Africa may perhaps throw light on, and be interpreted with due regard to, problems in South Africa. For similar reasons the investigations in South Africa arouse like hopes among archaeologists elsewhere.

As Prof. Dreyer points out, I suggested² that the South African Middle Stellenbosch is akin typologically to the East African Early Acheulean. I hasten to assure him that that 'correlation' was not necessarily one of time; I only wished to point out that the Middle Stellenbosch could scarcely be equated with the East African Chellean in type.

I am unable for two reasons to follow Prof. Dreyer's argument that if that correlation is valid then human history must have begun earlier in East than in South Africa. First, the beginnings of human history are far too nebulous in our present state of knowledge for claims of priority or contemporaneity to be made, and we are not even sure that the earliest men were tool makers. Secondly, we do know that man made implements long before any handaxe stage had been reached. Hence, typological differentiation or correlation of fairly advanced *coup de poing* industries scarcely concerns the beginnings of history anywhere.

Nor was it clear, when Prof. Dreyer stated that my correlation was based solely on typology, "deductions from which are vitiated by the