

MECHANISM OF THE ELECTROCHEMICAL REDUCTION OF SALICYLIC ACID\*

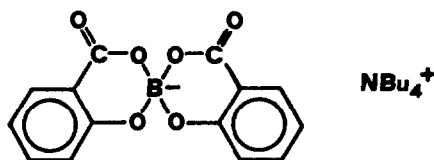
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The synthetic aspects of the electrochemical reduction of salicylic acid to salicylaldehyde have been quite extensively studied since early this century. Usually the work was done in aqueous media, and the presence of borate ions was found to be necessary to effect the reduction. However, neither the role of the borate ion nor the nature of the primary reaction steps in the reduction have yet been reported. We wish to throw some light on this aspect of the synthesis and report here some of our results obtained with DMF and aqueous systems.

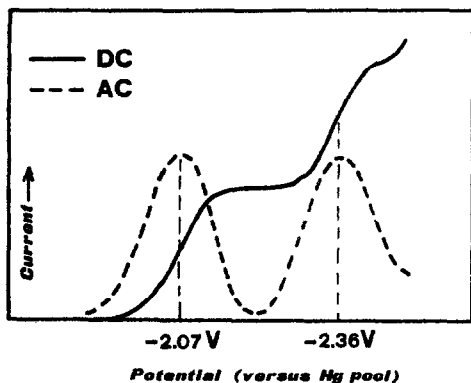
In agreement with previous work (1,2 and references cited therein) we have found that salicylic acid is itself not reduced in either water or DMF, except for the reductive discharge of hydrogen from the carboxylic acid group (3). This is in contrast to the conclusions of Hale and Hale (4), which are probably erroneous. On the other hand esters and the borate complexes of salicylic acid are electroactive. In our work the 1:1 and 1:2 complexes of borate and salicylic acid: MSB and DSB respectively, were prepared according to the method of Schäfer (5). The tetrabutylammonium salt of DSB was purified by fractional crystallisation and precipitation and analysed by IR, NMR, and microanalysis. These determinations were in agreement with the formula being:



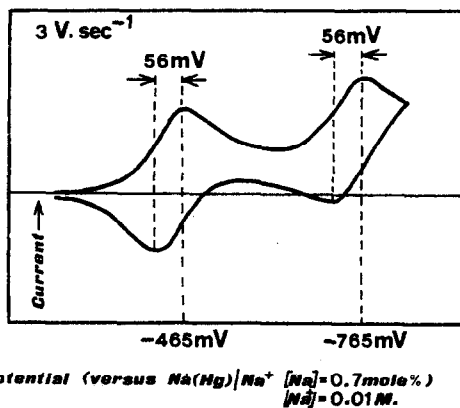
\* Taken from the thesis of J.Ch.Hofmann (in preparation)

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In DMF containing 0.1 M tetrabutylammonium bromide, MSB was reduced in a single one-electron polarographically reversible wave at  $-2.07$  V. (versus Hg pool). However, DSB (tetrabutylammonium salt) gave two waves at  $-2.07$  V. and  $-2.36$  V. respectively. AC and DC polarography and cyclic voltammetry (CV) showed that the two processes were reversible one-electron transfers.

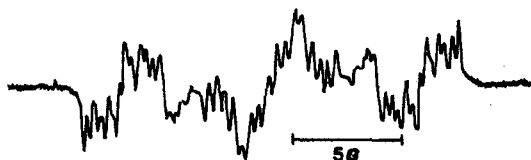


**Polarography of DSB in DMF.**

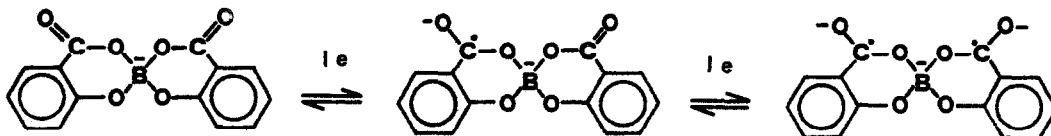


**Cyclic Voltammetry of DSB in DMF.**

The fact that MSB is reduced in a single one-electron step, while DSE goes in two one-electron steps, indicates that for DSB, localisation of the two electrons is not confined to just one of the salicylate moieties, but that one electron is added to each carboxyl group. The difference in potential between the two waves of DSB (290 mV.) can be attributed to the deactivation of the second carbonyl group due to inductive effects following the transfer of the first electron. The ESR Spectrum of the reduction intermediates, obtained by electrolysis within the cavity, confirmed that a radical species was always present. This suggests the formation of a di-anion radical and not a dianion.



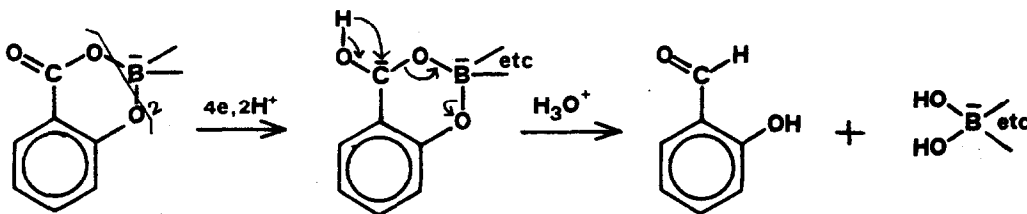
**ESR spectrum of DSB reduction product.**



The increase in the ease of reduction gained by forming the borate complexes is due to a lowering of the charge density on the carboxyl group. The increased reactivity can be compared to that of the esters *o*- and *p*-hydroxymethylbenzoate ( $E_{1/2}$  -1.63 V. and -1.99 V. respectively).

Addition of water to the DMF system increases the height of the first reduction wave of DSB together with loss of the second wave. In the limiting case of 100 mole % water the wave corresponds to the addition of four electrons.\* The AC polarography indicates that the transfer of two electrons is still reversible at a water concentration of 50 mole %. Beyond this concentration the reversibility is lost. The marked change in reversibility above 50 mole % water is interlinked with behaviour of the strong complex formed between water and DMF. Only at higher water concentrations does the mixed solvent become more strongly protic.

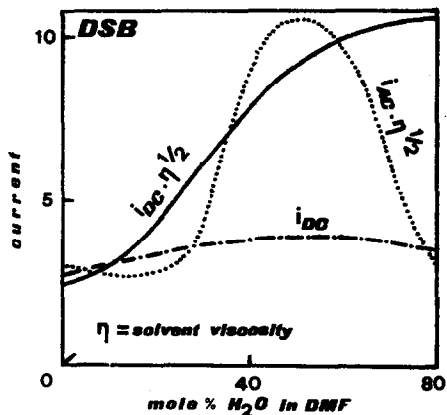
We therefore propose the following reaction path for the reduction of DSB in protic media:



The rate of decomposition of the reduced DSB in solution will determine the success in isolating the aldehyde either by trapping or in-situ extraction.

#### Acknowledgement

One of us (J.-Ch.H.) would like to thank Lonza AG for financial support.



**Dependence of polarographic currents (at first wave) on solvent composition.**

\* In order to compare the limiting currents at different water concentration it is necessary to correct for the accompanying viscosity change of the solvent.

References

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