

On the synthesis of salicylic acid by Hermann Kolbe.



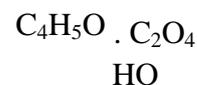
Hermann Kolbe (27-Sep-1818 – 25-Nov-1884)

Brief communication from H Kolbe

(Received 17-Dec-1859)

The observation made by Gerland six years ago that anthranilic acid is, upon exposure to nitrous acid, converted to salicylic acid, whereas the same conditions on 'Amidobenzoësäure' furnish the anthranilic isomer oxybenzoic acid led me first to the obvious supposition, that salicylic acid is an ether-carboxy similar in form to 'phenyl-oxydkohlensäure':

Ether-carboxy...



Phenyl-oxydkohlensäure (Salicylic acid)... $\text{C}_{12}\text{H}_5\text{O} \cdot \text{C}_2\text{O}_4$

HO

Another piece of evidence is the known decomposition of salicylic acid when heated with lime or glass powders in phenol and carbon dioxide.

I have expressed this view in a note of response to Gerland's paper, and since then have made many futile attempts at preparing salicylic acid directly from phenol and carbon dioxide. Those chemists who support that salicylic acid is, based upon Piria's investigation and other observations, a dibasic acid according to the formula: $2\text{HO} \cdot \text{C}_{14}\text{H}_4\text{O}_4$ will find that Mifslingen's experiments proceed and agree quite naturally. But I have never been able to reconcile myself with this view, and I even consider the existence of such a composite salicylic acid, for reasons I will explain later, theoretically impossible.

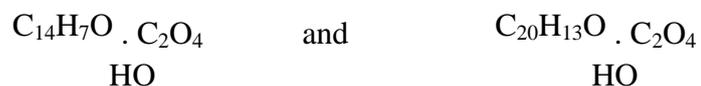
Still clinging to the idea that salicylic acid is one of the monobasic acids, and imbued with the correctness of the view that it was a carbonated phenol, I have recently been in communion with Lautemann over his previously reported attempts to synthesize salicylic acid from phenol and carbon dioxide.

We have found that the compound is not created by the exposure of carbon dioxide to sodium phenoxide, but that it is when one passes carbonic acid through phenol while sodium is dissolved therein that these three species unite under the confinement of hydrogen to give

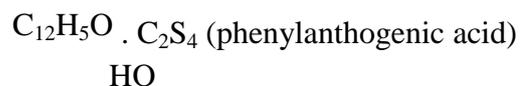
English translation of Kolbe's 1860 paper in Annalen der Chemie und Pharmacie on the synthesis of salicylic acid—now known as the Kolbe-Schmitt reaction

sodium salicylate. The aqueous portion from the reaction is then neutralized by the addition of hydrochloric acid to expel any unreacted phenol. The product is then boiled out of the aqueous portion and condensed to give a considerable amount of pure salicylic acid as crystals.

We have since engaged in applying the same procedure to cresol and thymol to achieve the homologous acids:



and we hope that in a similar manner from carbon disulfide and phenol we will obtain the compound:



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