Electrolytic Reduction of Saccharin. Part I. Electrolysis in Acid and Alkaline Solutions

By

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(Received February 17, 1932)

Not long ago B. Sakurai[1] reported that phthalimide easily undergoes reduction electrolytically, and that one of the two carbonyl groups changes first into the corresponding secondary alcoholic group and then into the methylene group, as is generally seen in the reduction of the carbonyl compounds. Judging from its analogous composition, saccharin may be expected to behave chemically in a similar manner, yet an attempt made by Remsen and Burton[2] to reduce it with tin and hydrochloric acid was reported to have ended in failure. The present authors thought it might be very interesting, therefore, to determine experimentally how saccharin differs from phthalimide in its behavior towards electrolytic reduction.

The electrolytic reduction of saccharin in an acid solution was observed to differ entirely from that in an alkaline solution, which splitt off the sulphonyl group from the benzene ring in the form of sulphurous acid and produced benzamide and its reduction products, such as benzaldehyde and hydrobenzoin. Reduction in an acid solution may be regarded to have taken place in such a way that the carbonyl group was transformed into the methylene group through the stage of the secondary alcohol group. Still, the intermediate hydroxybenzylsultam[3] itself could never be isolated, being always produced condensed with the ultimate reduction product, thus—

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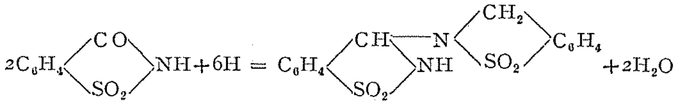
[1] Bull. Chem. Soc., Japan, **5**, 184 (1930).

[2] I. Remsen and M. Burton: Am. Chem. Jour. **11**, 403 (1889).

[3] The nomenclature proposed by P. Fritsch [Ber. **29**, 2290 (1896)] is used here because of its brevity.



$$2C_6H_4{<}\begin{matrix}CO\\SO_2\end{matrix}{>}NH+6H = C_6H_4{<}\begin{matrix}CH{-}N{<}\begin{matrix}CH_2\\SO_2\end{matrix}{>}C_6H_4\\SO_2\end{matrix}{>}NH+2H_2O$$

It is here to be noted that the same condensation product was also obtained by J. Koetschet[1] who, with the object of preparing saccharin, oxidized o-toluol sulphamide using p-toluol dichlorsulphamide as the oxidizing agent.

Experimental

I. Electrolysis was first conducted by taking a solution, which consisted of 50 c.c. of 15% sulphuric acid, 50 c.c. of alcohol and 5 grams of saccharin, as the catholyte and 15% sulphuric acid as the anolyte. A lead plate of 70 sq. cms. was used as the cathode, and a current of 5.5 amperes was passed at 15°—18° for 3 hours. The anode was also of lead. On electrolysing under agitation of the cathode solution, saccharin, at first suspended in the catholyte, gradually disappeared, and the solution, which had been pale yellow in colour, became colourless. The current was then cut, and the catholyte was nearly neutralized with caustic soda and evaporated to drive off alcohol. On the solution being cooled, a reduction product crystallized out. By purifying it by recrystallization from hot water a substance melting at 141° was obtained. It was analysed with the following results:

0.1169 gm. of the substance gave 0.2131 gm. CO_2 and 0.0397 gm. H_2O. 0.1000 gm. of the substance produced ammonia for neutralization of which 8.5 c.c. of $\frac{1}{14}$N-HCl was required.

	C	H	N
Found (%)	49.74	3.80	8.50
Calc. for $C_{14}H_{12}O_4N_2S_2$ (%)	50.00	3.60	8.30

Its molecular weight was found to be 345 (Calc., 336) by the ebullioscopic method, ethyl alcohol being used as the solvent.

0.0078 gm. of the substance in 12.0208 gms. alcohol raised the B. P. of alcohol by 0.002°.

It is soluble in alcohol, acetone, alkali and hot water; sparingly so in benzene, chloroform and ether. On further electrolytic reduction

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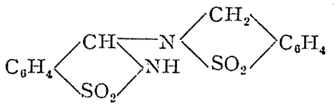
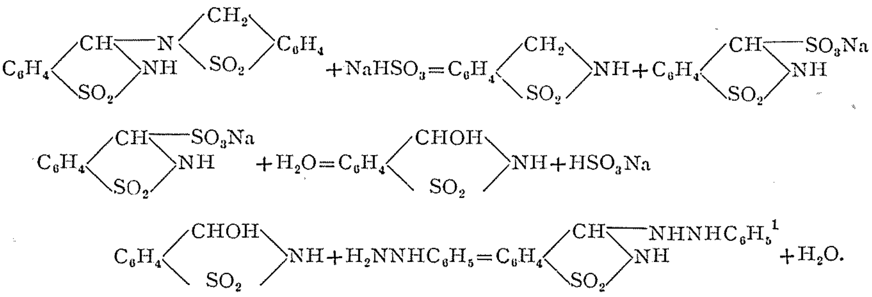
[1] J. and P. Koetschet: Helv. Chimi. Acta, **12**, 669 (1929).

it changes into benzylsultam and on oxidation into saccharin. When its alkaline solution is saturated with sulphurous acid gas and left to stand, benzylsultam crystallizes out. From the solution separated from the crystals of benzylsultam, a phenylhydrazine compound of hydroxybenzylsultam is easily obtainable as fine yellow needles by first neutralizing it with an acid and then treating it with phenylhydrazine. Judging from these properties and also from the results of analysis, the reduction product is evidently a condensation product of the formula,



Its reaction with phenylhydrazine may be conceived to proceed according to the following scheme:



In this electrolysis the concentration of acid and the current density do not much affect the reduction, but the temperature must always be maintained below 30°. The use of zinc, mercury and zinc amalgam as the cathode has no significant effect if the other conditions of electrolysis are not altered.

II. A series of electrolyses was now undertaken with the object of obtaining a still further reduced product by increasing both the current density and the concentration of acid and at the same time raising the temperature to 50°. The concentration of sulphuric acid was doubled and a current of 1 ampere/10 sq. cms. was passed for 2 hours. The catholyte after electrolysis was treated just in the same manner as in 1, and a substance crystallizing in needles and melting at 107° was obtained. It was analysed with the following results:

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[1] This phenylhydrazine compound was also prepared by Koetschet, who named it the phenylhydrazone of pseudo-o-sulphamidboenzaldehyde.

0.1261 gm. of the substance gave 0.2276 gm. CO_2 and 0.0483 gm. H_2O. 0.1151 gm. of the substance produced ammonia for neutralization of which 9.7 c.c. of $\frac{1}{14}$N-HCl was required.

	C	H	N
Found (%)	49.24	4.29	8.43
Calc. for $C_7H_7O_2NS$ (%)	49.70	4.10	8.30

It is soluble in alcohol, ether, acetone, chloroform and hot water, far less so in carbon bisulphide and benzene. When oxidized with potassium permanganate it changes into saccharin. All these properties well agree with those possessed by one of the decomposition products obtained from the above mentioned condensation product.

Whether the reduction goes on to benzylsultam or stops at the formation of the intermediate condensation product, chiefly depends on the temperature at which the electrolysis is carried out. This was confirmed by several experiments performed with the object of making this relation clear.

III. In all the experiments above described, hydroxybenzylsultam could, in no case, be obtained in the free state. The use of copper as the electrode was also found fruitless. Perhaps this is due to the fact that hydroxybenzylsultam and saccharin undergo reduction with nearly equal ease, and the former is very liable to enter into a condensation reaction with its reduction product. From such a point of view it was attempted to catch hydroxybenzylsultam in some combined form as quickly as it was formed, by electrolysing saccharin in the presence of phenylhydrazine. The conditions of electrolysis were the same as in 1. except the concentration of sulphuric acid, the percentage of which was lowered from 15% to 10%. About 3.5 grams of phenylhydrazine was added to the catholyte. As the electrolysis went on, a yellow substance began to separate out and accumulated in the cathode compartment. It crystallized from alcohol in fine yellow needles melting at about 197° and was identified as the phenylhydrazone of pseudo-o-sulphamidobenzaldehyde obtained by Koetschet[1]. When further electrolysed at a higher temperature (50°), the concentration of sulphuric acid and the current density being at the same time raised, as in II, it was readily reduced to benzylsultam completely.

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[1] loc. cit.

IV. Finally, electrolysis in an alkaline solution was carried out, 3% caustic soda solution being taken as the catholyte and a sodium carbonate solution as the anolyte. Both electrodes were of lead and a current of 3 amperes/70 sq. cms. was passed for an hour at 15°–18°. By treating the catholyte after electrolysis with chloroform, a quantity of white shining crystals melting at 127° was obtained with the material yield of 65%. On its properties being examined, the substance was found to be benzamide. It having been thus found that electrolysis in an alkaline solution splitt off the sulphonyl group from the benzene ring, the catholyte from which the benzamide had been extracted was acidified with hydrochloric acid, when a considerable evolution of sulphurous acid gas was recognized.

When the electrolysis was continued longer than an hour the catholyte began to evolve ammonia gas and at the same time to show the presence of benzaldehyde. It is hardly necessary to say that, as some of the benzaldehyde condenses into benzoin, reduction of the latter substance also takes place simultaneously so as to produce hydrobenzoin. Benzaldehyde was confirmed as its phenylhydrazone melting at 156° and hydrobenzoin as stilbene bromide melting at 237°.

The results of electrolytic reduction of saccharin in a neutral solution will be reported in the near future.