## Solubility of Stannous Oxide in Perchloric Acid

By MEL GORMAN AND PHILIP A. LEIGHTON

The purpose of this note is to present data on the solubility of stannous oxide in aqueous perchloric acid and to compare them with data on the solubility of this oxide in aqueous hydrochloric acid, which have recently been published by Garrett and Heiks.[1] Perchloric acid was chosen for the present study because the perchlorate ion is not capable of forming complexes with stannous ion.

**Reagents.**—Baker c. p. stannous oxide containing a small amount of stannic oxide impurity was used. No attempt was made to remove the impurity because it does not dissolve in the acid and in no other way interferes with the experiments. The perchloric acid solutions were prepared by dilution of the 60% reagent grade acid, and were titrated against sodium hydroxide solutions, which in turn had been standardized against potassium acid phthalate. The iodine solutions were standardized against special reagent grade arsenious oxide using starch indicator. All standardizations were performed in duplicate and agreed to within 0.1–0.2%.

**Procedure.**—Portions of stannous oxide were agitated by a shaking device in vessels containing perchloric acid of known concentrations, under an atmosphere of nitrogen. After an equilibrium period of from fifteen to twenty days at 25.0° the stannous oxide was allowed to settle and two duplicate aliquot parts of the solution were rapidly removed and placed in flasks containing carbon dioxide. They were immediately analyzed for stannous tin by titration against standard iodine using starch indicator under an atmosphere of carbon dioxide. These duplicate titrations agreed to within less than 0.3%.

### Results

The data are shown in Table I and Fig. 1. The solubilities were plotted on a large-scale graph and a smooth linear curve drawn to obtain the average solubility over the whole range studied. Each solubility measurement was compared with this average and showed the average deviation over the whole range to be ± 5%. In the range above 0.02 molar perchloric acid the average deviation is ±3%.

#### TABLE I
SOLUBILITY OF STANNOUS OXIDE IN PERCHLORIC ACID

| Initial moles of HClO₄/l. | Moles of SnO/l. | Initial moles of HClO₄/l. | Moles of SnO/l. |
|---|---|---|---|
| 0.0113 | 0.00318 | 0.0665 | 0.0276 |
| .0186 | .00890 | .0665 | .0278 |
| .0254 | .0124 | .0823 | .0353 |
| .0311 | .0126 | .0866 | .0353 |
| .0343 | .0149 | .0870 | .0384 |
| .0433 | .0179 | .0870 | .0374 |
| .0449 | .0176 | .1125 | .0480 |
| .0590 | .0257 | .1125 | .0471 |

(1) Garrett and Heiks, THIS JOURNAL, **63**, 562 (1941).

Inspection of Fig. 1 reveals that within the limits of experimental error the solubility of stannous oxide in perchloric acid is the same as in hydrochloric acid in the range where comparison is possible, i. e., up to 0.04 molar acid and 0.017 molar stannous tin. These facts are apparently the first evidence proving that there is little or no complex tin ion formation in the dilute concentration ranges of stannous ion and hydrochloric acid here considered. The few solubility measurements in solutions higher than 0.04 molar hydrochloric acid do not justify an accurate comparison with the solubility of stannous oxide in perchloric acid in this upper range.
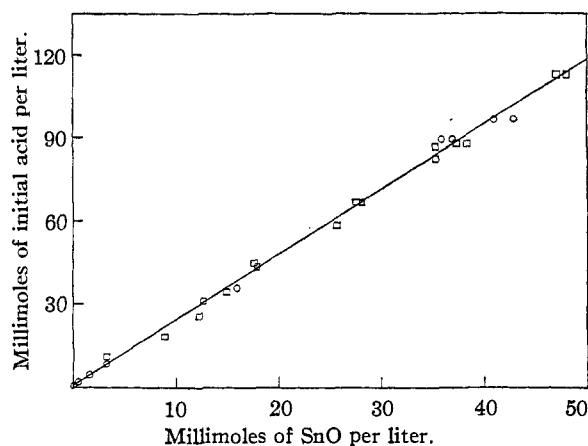


Fig. 1,—Solubility of SnO in acid: O, in HCl (Garrett and Heiks); □, in HClO₄; solid line, smoothed data of Garrett and Heiks.

It has long been known that stannous ion has a tendency to form complex ions with chloride ions at relatively high concentrations of the latter. Young's[2] conductivity investigations of one normal stannous chloride in varying hydrochloric acid concentrations between 0.25 normal and 7 normal indicate the existence of such complexes. More recently Prytz[3] has attempted to interpret his potentiometric data in dilute stannous chloride solutions containing hydrochloric acid at various concentrations by postulating the existence of complex stannous ions. He reports that 57% of stannous tin is in the form of stannous ion and 32% as $SnCl^+$ in a 0.01 molar stannous chloride solution containing hydrochloric acid at 0.01 molar. However, a calculation using the equilibrium constant for the hydrolysis of stannous ion[4] shows that in the above solution the

(2) S. W. Young, ibid., **23**, 20 (1901).
(3) M. Prytz, Z. anorg. allgem. Chem., **172**, 147 (1928).
(4) Gorman, THIS JOURNAL, **61**, 3342 (1939).

stannous ion is about 30% hydrolyzed to SnOH$^+$. Obviously these figures of Prytz cannot be correct.

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## An Oxidation Product of $\Delta^{9,10}$-Octalin

BY G. CHRIS HARRIS

In a recent communication[1] the preparation of an unsaturated octalone-1 by selenium dioxide oxidation was reported. On the basis of the maximum at 243 m$\mu$ in the ultraviolet absorption spectrum of this substance, the suggestion was made that the double bond should be written at 8,9 instead of the previously postulated 9,10-position. It was pointed out,[2] however, that all of the $\alpha,\beta$-unsaturated ketones whose spectra had been determined had an exocyclic double bond (as $\Delta^{8,9}$-octalone) and none of the $\Delta^{9,10}$-octalone type had been measured. This evidence, therefore, could not be considered conclusive until further data were available.

We now have some evidence of a different nature which favors the 9,10-position for the double bond. Kharasch and Tawney[3] reported the 1,4-addition of methylmagnesium chloride to isophorone in 82.5% yield when 1.0 mole per cent. of cuprous chloride is present. This reaction was repeated successfully and then was tried under the same conditions on the unsaturated octalone. No oxime-forming material was found in the reaction mixture. The distilled product of the reaction readily absorbed bromine in carbon tetrachloride solution without the evolution of hydrogen bromide.

The failure to obtain a ketone in this reaction indicates that no 1,4-addition took place. The reaction of the product with bromine is indicative of the unsaturated alcohol or hydrocarbon formed by 1,2-addition rather than the saturated ketone which would result from the 1,4-addition. It is more difficult to explain the lack of 1,4-addition if the octalone is the $\Delta^{8,9}$-isomer since the double bond appears to be less hindered.

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(1) W. P. Campbell and G. C. Harris, THIS JOURNAL, **63**, 2721 (1941).
(2) Robert Burns Woodward, ibid., **64**, 72, 76 (1942).
(3) Kharasch and Tawney, ibid., **63**, 2308 (1941).

## Sterols. CXXXIV. Some Observations on the Structure of Ouabain

BY RUSSELL E. MARKER, D. L. TURNER, THOMAS S. OAKWOOD, EWALD ROHRMANN AND PAUL R. ULSHAFER

When heptaacetyldesoxydihydroouabain is subjected to acetolysis it loses the sugar residue and three acetoxy groups. One carbon atom is also eliminated as formaldehyde.[1,2] To explain this reaction Fieser[3] assumed that ring B had become aromatic. On this basis he assigned provisional formulas to ouabain and its derivatives. A careful study of the existing literature and some new experiments with neoergosterol and related compounds convince us that these formulas cannot be correct. The pertinent facts both old and new are given in Table I.

TABLE I

| Neoergosterol (has ring B aromatic) | Acetolysis product from ouabain |
|---|---|
| Readily dehydrogenated | Cannot be dehydrogenated |
| Cannot be hydrogenated | Hydrogenated in acetic acid |
| Cannot be oxidized to a ketone with chromic anhydride | Oxidized to a ketone with chromic anhydride |

5,7,9-Estratrienol-17 (has ring B aromatic, cannot be hydrogenated)

Equilenin (has rings A and B both aromatic), ring A hydrogenated in acetic acid; ring B cannot be hydrogenated

Theelin (has ring A aromatic), ring A is reduced in acetic acid

Trianhydrostrophanthidin (has ring B aromatic), ring B cannot be reduced

Dehydroneoergosterol (has rings A and B aromatic), only ring A is reduced in acetic acid

All of these facts indicate that ring A in the acetolysis product and not ring B has become aromatic. It thus seems improbable that Fieser's formulas for ouabain and its derivatives can be correct. At present there is not sufficient evidence available to determine the structure of ouabain.

We wish to thank Parke, Davis and Company for their assistance.

### Experimental

**Hydrogenation of Neoergosterol.**[4]—A mixture of 10 g. of neoergosterol, 500 cc. of glacial acetic acid and 2 g. of platinum oxide catalyst was shaken with hydrogen at room temperature and 45 pounds. After about thirty minutes,

(1) Jacobs and Bigelow, J. Biol. Chem., **96**, 647 (1932).
(2) Jacobs and Bigelow, ibid., **101**, 15 (1933).
(3) Fieser and Newman, ibid., **114**, 705 (1936).
(4) Cf. Bonstedt, Z. physiol. Chem., **185**, 165 (1929).