may have been due to the hydration of the silver alone, and hence there is no evidence of the hydration of the calcium ions. However, it is not proved that they are not hydrated.

(4) By the electrolysis of a solution of silver nitrate in a mixture of pyridine and water, it was found that a large proportion of the pyridine present was combined with the silver ions.

THE BASIC PROPERTIES OF OXYGEN: ADDITIVE COMPOUNDS OF THE HALOGEN ACIDS AND ORGANIC SUBSTANCES CONTAINING OXYGEN.

BY D. McINTOSH.

Received March 10, 1906.

THE basic properties of oxygen, as exhibited in some organic compounds at low temperatures, have been discussed in a number of articles, and the quadrivalency of oxygen has been suggested to explain the constitutions of the compounds formed. The six principal classes of organic bodies—the alcohols, ethers, ketones, aldehydes, acids and esters—unite with the halogens, and the substances formed have been investigated. Only the first three classes are known with certainty to give compounds with the halogen acids, so that an examination of typical bodies of the last three classes, described in the following pages, may not be without interest.

The halogen acids were prepared in the ordinary way; the aldehyde was made from paraldehyde, the acetic acid purified by several crystallizations, and the ethyl acetate distilled from phosphorus pentoxide.

The compounds were formed with the evolution of large amounts of heat, were crystalline, and had sharp melting-points. They dissolved easily and formed supersaturated solutions in the acid from which they were formed.

Compounds with Hydrochloric Acid.—Aldehyde at —80° C. was quickly changed to paraldehyde by the addition of a few drops of the liquefied acid. The paraldehyde dissolved in an excess of the halogen·acid, and a compound melting at —18° separated out on standing. The analyses gave 54.1, 52.4, 53.3 per cent. acid, while $(CH_3CHO)_2(HCl)_3$ contains 55.3 per cent.

Acetic acid gave a product which melted at —53°, and was found to contain 45.7 and 44.5 per cent. of the halogen acid.

$(CH_3COOH)_2(HCl)_3$ requires 47.7 per cent. Ethyl acetate hydrochloride melts at —75° and gave on analysis 47.3 and 46.5 per cent. of acid. Its probable formula is $CH_3COOC_2H_5 2HCl$, which contains 45.3 per cent. acid.

For comparison, a compound of methyl alcohol and hydrochloric acid was made. It melted at —64°, and contained 46.4 and 44.6 per cent. of acid, while $(CH_3HO)_3(HCl)_2$ contains 43.2 per cent. This product was washed with the liquefied acid, and the high percentage of acid found is due to this.

Compounds with Hydrobromic Acid.—In hydrogen bromide the acetaldehyde was transformed into paraldehyde, which dissolved. A compound melting at —15° and showing on analysis 69.7 and 71.9 per cent. of acid was formed, so that the most likely formula is $(CH_3CHO)_2(HBr)_3$, which requires 73.4 per cent. acid.

Acetic acid does not unite with hydrogen bromide or iodide at low temperatures, but compounds of ethyl acetate and the acids are easily made. The analytical results for the hydrobromic acid product which melted at —40° were: 51.4, 52.0, 52.0 and 52.5 per cent. HBr. $(CH_3COOC_2H_5)_2(HBr)_3$ and $CH_3COOC_2H_5HBr$ contains 58.0 and 47.9 of acid respectively, so that the first formula is to be preferred.

Compounds with Hydriodic Acid.—Paraldehyde and hydriodic acid give a compound melting at —32°. It contained 65.7, 66.4, and 66.0 per cent. acid, while $(CH_3CHO)_3(HI)_2$ contains 66.0 per cent.

The ethyl acetate-hydriodic acid combination melted at —23° and contained 56.3 and 57.1 per cent. acid. Its formula is $CH_3COOC_2H_5HI$, which contains 59.3 per cent.

In the following table are placed the formulas derived from the analytical data given above and the approximate temperatures at which these bodies melt. The ethyl acetate compounds act like those previously described, *i. e.*, the lower the temperature at which they melt, the greater the amount of acid required to "saturate" the oxygen, while the aldehyde compounds vary irregularly. A hydroxyl oxygen atom unites with one, and a ketonic oxygen with two atoms of a halogen. If the oxygen atoms are without influence on each other, we should expect ethyl acetate to unite with three halogen atoms, and this we find to be the case,

---

[1] J. Chem. Soc. 85, 919 (1904); 85, 1098 (1904); 87, 784 (1905); This Journal, 27, 26 (1905); 27, 1013 (1905).

$CH_3COOC_2H_5Cl_3$ and $CH_3COOC_2H_5Br_3$ being formed. This regularity is not shown in the case of the halogen acid compounds.

COLLECTED RESULTS.

Compounds.	M. P.
$(CH_3HO)_3(HCl)_2$	—64°
$(CH_3CHO)_2(HCl)_3$	—18°
$(CH_3COOH)_2(HCl)_3$	—53°
$(CH_3COOC_2H_5)(HCl)_2$	—75°
$(CH_3CHO)_2(HBr)_3$	—15°
$(CH_3COOC_2H_5)_2(HBr)_3$	—40°
$(CH_3CHO)_3(HI)_2$	—32°
$CH_3COOC_2H_5HI$	—23°

No attempt has been made to indicate the constitutions of these bodies, which may be done by making the oxygen a tetrad. That these compounds differ in many respects from the so-called molecular combinations (salts with water of crystallization etc.), I shall attempt to show in another paper.

MCGILL UNIVERSITY, March, 1906.

THE CONSTITUTION OF CERTAIN NATURAL SILICATES.[1]

BY H. C. MCNEIL.

Received March 6, 1906.

THE representation of natural silicates as substitution products of simple silicic acids, was begun by Professor Clarke about 1886 and has been developed continuously ever since. A formula to be satisfactory is expected to accord, with all known facts of the genesis, alterations, artificial syntheses and transformations, as well as physical and chemical properties of the mineral. The chief lines of laboratory work have been fractional analyses by several methods, and varied substitution reactions.

The graphical representations of Butureanu,[2] Vernadsky,[3] and Simmonds,[4] may be mentioned as the more recent attempts in this line.

The present investigation was carried out in the Chemical Laboratory of the United States Geological Survey, under the supervision of Professor Clarke, in the development of his theory

---

[1] From a thesis submitted for the degree of Doctor of Philosophy, George Washington University, 1905.

[2] Bull. soc. sci. fis. Bucuresci, 1896, 60-73, 117-124, 129-139, 254-279.

[3] Z. Kryst. Min. 34, 37-66 (1901).

[4] J. Chem. Soc. 1903, 1449-1469, and Ibid. 1904, 681-685.