From the above it is evident that Dr. Lederer experimented with compounds of tungsten, similar to those described in my paper, with a view to their use in the incandescent lamp industry, but did not isolate the compounds nor determine their composition by analysis. This was the main purpose of my paper.

JOHN B. EKELEY.

PARIS, January 10, 1910.

THE BASIC PROPERTIES OF OXYGEN: COMPOUNDS OF DIMETHYLPYRONE AND THE HALOGEN HYDRIDES.

BY D. McINTOSH.

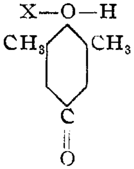
Received February 12, 1910.

In 1899 Collie and Tickle[1] produced crystalline compounds by the addition of various acids to dimethylpyrone. They showed that neither water nor carbonic acid was eliminated by this treatment and that a simple ratio existed between the molecular quantities of the two reacting substances. To explain their results in terms of the current valency theory, they advanced the view suggested many years earlier by Friedel, that in certain compounds oxygen may act as a tetravalent element (the oxonium theory).

Since Collie and Tickle's paper appeared, additive complexes of substances containing oxygen have been widely studied by Baeyer and Villiger, Kehrmann, Hantzsch, Werner and many others.

The salts of dimethylpyrone have naturally undergone careful investigation. Collie and Steele[2] have produced compounds with iodine and hydriodic acid, Weinland and Reischle[3] combinations with hydrofluoric acid, while Plotnikov[4] has described basic and acid salts with chloro- and bromo-acetic acids. The constitutions of these compounds are explained by the assumption of a tetravalent oxygen atom or by the subsidiary bonds according to Werner's theory.

In Collie's first paper dimethylpyrone was represented as a ring containing two divalent oxygen atoms, which for discussion may be termed the ethereal and the carbonyl oxygen atoms. The salts of dimethylpyrone were supposed to have the acid attached to the ethereal oxygen atom, although no reason for its selection was given; and the compounds were represented as



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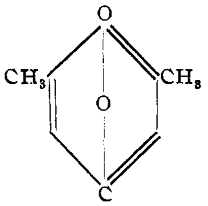
[1] *J. Chem. Soc.*, **75**, 710.

[2] *Ibid.*, **77**, 1114 (1900).

[3] *Ber.*, **41**, 3671 (1908).

[4] *Ibid.*, **42**, 1154 (1909).

Recently Collie[1] has changed his views regarding the composition of the pyrone and its salts. The former is supposed to have a tetravalent oxygen atom, and in the latter the acid is attached to the carbonyl oxygen atom. The constitutions given are:



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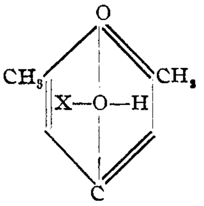

This hypothesis is strengthened by the work of Homfray[2] and also by the spectroscopic measurements of Baly.[3] On the other hand, Willstäter and Pummerer[4] give reasons why the pyrone itself cannot have a tetravalent oxygen atom and inferentially why its salts cannot have the formulas attributed to them.

In a former paper[5] I attempted to show that some of the compounds regarded by Baeyer and Villiger as containing tetravalent oxygen atoms were merely cases of solid solution, while others formed from hydroferrocyanic acid and the alcohols did not differ in structure from salts with alcohol or water of crystallization. Dimethylpyrone, like ferrocyanic acid, is a solid at ordinary temperatures, and since its salts might be looked on as pyrone with "acid of crystallization," I have examined some of its compounds over a considerable temperature range.

Materials.—The dimethylpyrone was purchased from Merck. No process of purification was thought necessary as its salts of the halogen acids were identical with those described by Collie and Tickle. The halogen hydrides were prepared and liquefied in the ordinary way. The hydrogen fluoride was obtained by distillation of a pure solution of the acid, and experiments with it were carried out in platinum vessels.

Since the formation of compounds is often indicated by electrical conductance in solution, measurements of dimethylpyrone in hydrogen bromide at —78° and in hydrogen chloride at —100° were made. The results are given in the tables and shown in the diagram:

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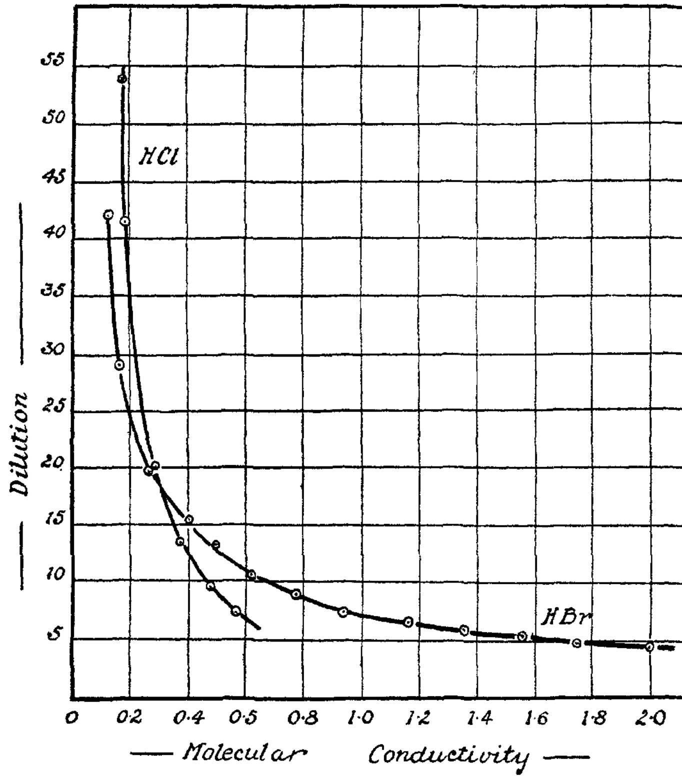
[1] *J. Chem. Soc.*, **85**, 973 (1904).

[2] *Ibid.*, **87**, 1443 (1905).

[3] *Ibid.*, **96**, 144 (1909).

[4] *Ber.*, **37**, 3740 (1904); **38**, 1461 (1905).

[5] THIS JOURNAL, **30**, 1097 (1908).



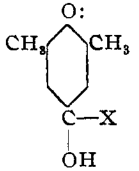
Hydrochloric acid.

Dilution.	Molecular conductance.
93·0	0.18
53·8	0.18
41·4	0.19
20.0	0.29
13·3	0.38
9·6	0.48
7·4	0·57

Hydrobromic acid.

Dilution.	Molecular conductance.
42.0	0.13
29.2	0.17
19·5	0.27
15·4	0.41
13·3	0.49
10.6	0.62
9·0	0.78
7·5	0·94
6.7	1.16
5·9	1·36
5·4	1·56
4·9	1·75
4·3	2.05

Dimethylpyrone itself cannot be looked on as an electrolyte. It must unite with the hydrobromic acid, otherwise the conduction of electricity would be impossible. The union cannot take place with a halogen and hydroxyl attached to the carbon, as suggested by Werner, for this compound



should not be ionized. The pyrone moves to the cathode during electrolysis, so the halogen is not attached to the oxygen by a double bond. Further, since the molecular conduction increases with concentration—as it does with all substances containing oxygen and nitrogen in these solvents—complex ions must be formed.[1] We may thus expect compounds in which the pyrone and acid are not present in equimolecular proportions.

Hydrochloric Acid Compounds.—A solution of dimethylpyrone in aqueous hydrochloric acid was kept in a vacuum desiccator till dry. It contained 22.6 per cent. acid and was, therefore, $C_7H_8O_2HCl$. Another specimen, dried between filter papers, gave 19.2 per cent. acid, corresponding to $C_7H_8O_2HCl.2H_2O$. These compounds were first prepared and described by Collie and Tickle.

Dimethylpyrone dissolves readily in liquefied hydrogen chloride with an evolution of heat, noticeable, but small compared with that given by ether, etc. A crystalline substance soon separates out, which melts sharply at —25°. Analyses of different preparations gave 42.6, 45.5, 44.1 and 42.7 per cent. acid. $C_7H_8O_2.2HCl$ contains 36.4, $C_7H_8O_2.3HCl$, 46.9 per cent.

Evidence of the existence of a more complex compound with a much lower melting point was obtained. The difficulty of removing the excess of acid was so great that this body was not examined further.

Hydrobromic Acid Compound.—From an aqueous solution of hydrobromic acid and dimethylpyrone compounds containing from 39.3 to 40 per cent. acid were produced. By dissolving the pyrone in the anhydrous acid and allowing the excess to evaporate salts with 38.9, 39.2, 38.4, 39.3 per cent. acid were made at various times. $C_7H_8O_2HBr$ contains 39.5 per cent. acid (Collie and Tickle). In anhydrous hydrogen bromide dimethylpyrone forms an oily liquid which dissolves easily. At the saturation point a compound probably containing one molecule of acid appears and this floats on the hydrobromic acid and dissolves but slowly. When the saturated solution is allowed to stand or when a crystal of the pyrone is added quickly with a stirrer, prismatic crystals (probably orthorhombic) with faces appear. These crystals give, on analysis:

Sample I,	74.7; 75.1 per cent. acid.
Sample II,	74.2; 75.1 per cent. acid.
Mean,	74.8 per cent. acid.

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[1] Steele, McIntosh and Archibald, *Z. physik. Chem.*, 52, 129 (1906).

This compound is doubtless $C_7H_8O_2 4HBr$, which contains 72.3 per cent. When warmed, the tetrahydrobromide melts sharply at —59°, the excess of acid quickly evaporates, and a solid reappears. This substance has a high vapor pressure and when "dried" at —35° contains 59.5, at —13° 53.2 per cent. acid, which corresponds to $C_7H_8O_2 2HBr$. It melts at —2° and is converted into the compound containing one molecule of acid. Vapor pressure measurements have failed to show the existence of a compound containing three molecules of acid.

Hydriodic Acid Compounds.—Dimethylpyrone dissolves, but less readily, in hydrogen iodide than in the bromide, and at a low temperature crystals separate out. These contain 83.3, 83.6 and 84.6 per cent. acid in three preparations, while $C_7H_8O_2.4HI$ has 82.2 per cent.

At —42°, $C_7H_8O_2.4HI$ melts and a substance with 69.8 per cent. acid separates, which in its turn liquefies at +7° and yields $C_7H_8O_2HI$. A compound of one molecule pyrone and two of hydrogen iodide contains 67.4 per cent. acid.

Hydrofluoric Acid Compounds.—Since fluorine does not unite directly with oxygen, oxonium compounds with hydrofluoric acid should prove of the greatest interest. Landolph[1] claims to have produced two substances in which hydrogen fluoride was united with acetone, and quite recently Weinland and Reischle[2] describe two dimethylpyrone hydrofluorides. The formula $C_7H_8O_2.3HF.0.5H_2O$ is given to one prepared from the aqueous acid, the other from an alcoholic solution is represented as $C_7H_8O_2 3.5HF 0.5H_2O$.

Stable compounds of pyrone and hydrofluoric acid are not easy to prepare. In one experiment an aqueous solution of acid and dimethylpyrone was kept over sulphuric acid and potash in a vacuum desiccator. When dry the salt contained 20.3 per cent. acid. After two weeks the acid content had fallen to 15.1 per cent.; two weeks later to 13.1; and after standing two months longer, only 10.7 per cent. acid remained.

A crystalline preparation, made with a large excess of acid, when dried between filter papers, held 37.7 per cent.; after two weeks in a desiccator this was reduced to 30.8 per cent. acid.

A third sample, made by mixing pyrone and acid in approximately molecular proportions, gave, when dried, 14.9 per cent. acid; after two weeks further drying, 13.9 per cent., which corresponds to the formula $C_7H_8O_2HF$. But after five months the acid had fallen to 9.6 per cent. If compounds of dimethylpyrone and hydrofluoric acid are formed they are neither so simple nor so stable as those with the halogen hydrides.

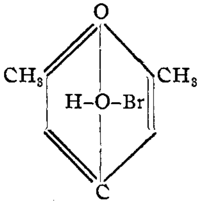
[1] *Compt. rend.*, 86, 1463; 96, 580.

[2] *Loc. cit.*

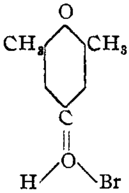
NOTE.—Anhydrous hydrofluoric acid is unlike the halogen hydrides. When treated with ether, acetone, etc., much less heat is evolved and compounds, if formed, do not crystallize out easily.

We have seen that hydrobromic acid unites with dimethylpyrone to give three stable compounds containing one, two and four molecules of acid. Since hydrobromic acid does not polymerize even when liquefied, any theory to explain the linking of the acid in the simplest compound should apply equally well to the others. We may regard these additive compounds as pyrone with "acid of crystallization," or we may ascribe formulas to them in which oxygen has a higher valency than two.

If we accept Collie's representation of the constitution of dimethylpyronehydrobromide,



it is difficult to give a satisfactory explanation of the formation of the other salts, unless we admit the possibility of the linking between the two oxygen atoms being broken at such a low temperature. But if we regard the dimethylpyrone itself as a substance with two divalent oxygen atoms we may represent the three salts as



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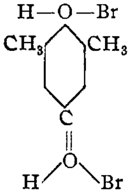

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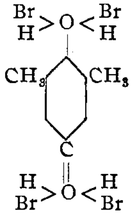

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the first containing one, the second two tetravalent, and the third three hexavalent oxygen atoms.

In the most complex salt the oxygen is supposed to function as a hexad, and this may be objected to as unusual and unnecessary. Yet the same arguments advanced for the tetravalency of oxygen apply equally strongly to its hexavalency here; and the position of this element in the sixth column of the periodic table permits the view that its valency may vary as does that of sulphur, selenium and tellurium.

ELEMENTARY ANALYSIS BY MEANS OF A CALORIMETRIC BOMB.

BY HAROLD L. HIGGINS AND ALICE JOHNSON.

Received January 24, 1910.

Since the complete oxidation of organic material, with the quantitative conversion of carbon to carbon dioxide, and of hydrogen to water, presents the greatest difficulty in elementary organic analysis, it is not surprising