

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA]

### ZIRCONYL CITRATE

BY F. P. VENABLE AND R. A. LINEBERRY<sup>1</sup>

Received June 7, 1922

The formation of a zirconium ammonium citrate has been reported by Harris.<sup>2</sup> On slowly adding an ammonium citrate solution to one of zirconyl chloride a curdy white precipitate was formed which was soluble in excess of the precipitant. It was washed with hot water, dried at 100° and analyzed. The ammonia was driven off only by boiling with sodium hydroxide. Analyses yielded 42.40% of zirconium and 11.92% of ammonia, which he stated corresponded with the formula  $Zr_2 \cdot C_6H_5O_7 \cdot (NH_4)_3$ , a surprising formula when the respective valences are considered.

It seems unnecessary to criticise this experiment in detail but it is quite important to repeat it, since it is the only reference in the literature to the formation of a compound of zirconium and citric acid. Carrying out the experiment as described in the article the precipitate was obtained and from it some ammonia could be liberated. The washings also yielded ammonia on treatment with sodium hydroxide. After a number of washings both precipitate and washings proved to be ammonia-free. Repetition of the experiment gave the same results. The conclusion was reached that the curdy precipitate retained some ammonium chloride which was gradually washed out and that no double citrate is formed in this way.

As stated, the precipitate is soluble in excess of ammonium citrate. A concentrated solution was prepared and placed over a drying agent, but no separation of a definite compound could be observed, the solution gradually becoming cloudy and leaving finally a jelly-like mass. Citric acid alone gives a similar precipitate with a solution of zirconyl chloride, also soluble in excess, and the solution evaporated in the same way gave a similar resulting mass. The solubility of moist zirconyl hydroxide, precipitated cold, in a normal solution of citric acid was found to be a little under 4 g. in 100 cc. Several attempts at forming the double citrate with potassium failed.

A 0.1 *N* solution of zirconyl chloride was precipitated by the slow addition of a 0.1 *N* solution of citric acid. In several experiments it was found that about 160 cc. of the acid was required for the complete precipitation of the zirconium in 100 cc. of the zirconyl chloride. The precipitate was washed free from acid, dried at 80° until the weight was constant and the zirconia weighed after ignition. The precipitation was made as quickly as possible after dissolving the zirconyl chloride so as to limit

<sup>1</sup> From a thesis presented in partial fulfilment of the requirements for the degree of Bachelor of Science.

<sup>2</sup> Harris, *THIS JOURNAL*, 20, 871 (1898).

the hydrolysis of the latter as much as possible. The analytical results show small variations which may be attributed to a slight hydrolysis. In seven experiments the percentages of zirconium dioxide present were as follows: 44.91; 44.84; 45.38; 45.79; 46.32; 45.47; 44.06. An increase in zirconium oxide indicates increased hydrolysis. The percentage of the dioxide in the substance  $(\text{ZrO})_3(\text{C}_6\text{H}_5\text{O}_7)_2$  is 45.80. The precipitate is, therefore, apparently the normal zirconyl citrate. It must be borne in mind that the loss of some zirconia is very difficult to avoid when it is ignited in the presence of organic matter.

When the zirconyl chloride solution was boiled for some time so as to bring about a far-reaching hydrolysis and the citric acid added to this, the resulting percentages of zirconium dioxide in four experiments were: 57.19; 57.37; 57.21; 57.20. These show a fairly definite resulting compound. The basic zirconyl citrate  $3 \text{ZrO}(\text{OH})_2 \cdot (\text{ZrO})_3(\text{C}_6\text{H}_5\text{O}_7)_2$ , contains 57.13% of the dioxide.

### Summary

1. No double citrate as reported by Harris was formed, nor was a double citrate with potassium obtained.
2. Zirconyl citrate,  $(\text{ZrO})_3(\text{C}_6\text{H}_5\text{O}_7)_2$ , was prepared. It is easily hydrolyzed.
3. Basic zirconyl citrate,  $3 \text{ZrO}(\text{OH})_2 \cdot (\text{ZrO})_3(\text{C}_6\text{H}_5\text{O}_7)_2$ , was also prepared.

CHAPEL HILL, NORTH CAROLINA

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

## VAPOR DENSITIES AT LOW PRESSURES AND OVER AN EXTENDED TEMPERATURE RANGE. I. THE PROPERTIES OF ETHYLENE OXIDE COMPARED TO OXYGEN COMPOUNDS OF SIMILAR MOLECULAR WEIGHT

BY O. MAASS AND E. H. BOOMER

Received June 15, 1922

### Introduction

This paper is the first of a series dealing with the vapor densities of a number of organic compounds. The densities dealt with are measured over a considerable temperature range and at various pressures with a view to bringing out the effect of the attracting forces of the molecules for one another and comparing other physical properties which are also influenced by these forces. Ethylene oxide is one of the substances which has been examined so far and since a number of its physical properties had to be determined, these are included in this paper together with those