

are due to this company for permission to publish these results, and to Mr. K. D. Ashley for his cooperation in the work.

Summary

A reaction not previously reported has been found to take place between cyanamide and cyanide, resulting in the formation of an intermediate compound which can be hydrolyzed to oxalate. The velocity of this reaction is dependent on hydrogen-ion concentration.

Autoclaving calcium cyanide and calcium cyanamide with water produces calcium carbonate, calcium oxalate and a solution of calcium formate. Replacing the water with calcium formate solution results in increased yields of oxalate.

AMERICAN CYANAMID COMPANY
535 FIFTH AVENUE, NEW YORK CITY

ZIRCONIUM. II. ZIRCONIUM OXALATE AND DIPHENYLDINITROGEN ZIRCONIUM

BY HOWARD S. GABLE

RECEIVED JANUARY 19, 1931

PUBLISHED APRIL 6, 1931

Zirconium Oxalate

The fact that an insoluble precipitate was obtained upon the addition of oxalic acid or ammonium oxalate to solutions of zirconyl salts has been known since 1820. Since that time a number of investigations have been made concerning various compounds containing zirconium and the oxalate group, but so far as can be determined there seems to have been no success when efforts were made to obtain the normal zirconium oxalate $Zr(C_2O_4)_2$. The marked success with which the author has prepared other normal zirconium compounds in methyl alcoholic solutions suggested that the oxalate might be prepared in a similar manner.

A methyl alcoholic solution of zirconium tetrachloride was treated with a methyl alcoholic solution of oxalic acid. A reaction took place at once with the formation of a white gelatinous precipitate. This was filtered off, washed, dried and analyzed.

Anal. Calcd. for $Zr(C_2O_4)_2$: Zr, 34.80. Found: Zr, 35.08.

The two figures are close enough together to establish the identity of the compound.

The effects of a number of common solvents were observed. They are given below in table form. It is worthy of note that the normal zirconium oxalate is quite soluble in water, quite contrary to what might be expected from the literature, since the basic salts investigated by other workers are noted for their insolubility.

Diphenyldinitrogen Zirconium

The formation of a precipitate upon the addition of aniline to a solution of a zirconium salt has been reported by Alice M. Jefferson.¹ She states that the addition of aniline is accompanied almost immediately by a separation of a beautiful white gelatinous precipitate. The results indicated that the reaction was quantitative. No analytical results as to the composition were given.

Mathews² had reported a few years earlier on the formation of an addition compound between aniline and zirconium tetrachloride when aniline was added to an ethereal solution of the zirconium compound. This was a gray precipitate corresponding to the formula $ZrCl_4 \cdot 4C_6H_5NH_2$.

The object of this investigation was to repeat the work by Jefferson, to determine the composition of the precipitate, and to carry out the reaction in methyl alcoholic solution.

An investigation proved that the precipitates obtained in alcoholic and water solutions were identical. The work carried out in methyl alcoholic solution is given below.

An excess of aniline was added to a dilute solution of zirconium tetrachloride in methyl alcohol, and the mixture allowed to stand for several days. On examination a voluminous precipitate was found which was filtered off and washed with methyl alcohol. The filtrate contained an excess of hydrochloric acid, showing that a replacement and not addition reaction had taken place. After drying the precipitate for some time it was analyzed.

Anal. Calcd. for $(C_6H_5N)_2Zr$: Zr, 33.37; N, 10.25. Found: Zr, 33.34; N, 10.40.

These figures indicate that the reaction took place according to



The solubility of the diphenyldinitrogen zirconium was observed in a number of solvents. These are given below with the solubilities of the oxalate.

Solvent	$Zr(C_2O_4)_2$	$(C_6H_5N)_2Zr$
CCl_4	Insoluble	Insoluble
CS_2	Insoluble	Insoluble
C_2H_5OH	Insoluble	Insoluble
CH_3OH	Insoluble	Insoluble
NH_4OH	Insoluble	Insoluble
HCl	Insoluble	Insoluble
$C_6H_5NH_2$	Slightly soluble	Insoluble
HCOH	Reaction	Reaction
H_2O	Very soluble	Insoluble
CH_3COOH	Slightly soluble	Insoluble
$(CH_3)_2CO$	Slightly soluble	Insoluble
HNO_3	Insoluble	Soluble

The reaction was quantitative.

¹ Jefferson, *THIS JOURNAL*, **24**, 540 (1902).

² Mathews, *ibid.*, **20**, 815 (1898).

Summary

1. The use of methyl alcoholic solutions allows compounds of zirconium to be prepared without danger of hydrolysis.
2. The normal zirconium oxalate, $Zr(C_2O_4)_2$, was prepared and described.
3. Diphenyldinitrogen zirconium, $(C_6H_5N)_2Zr$, was prepared and described.

3950 WALNUT STREET
KANSAS CITY, MISSOURI

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]
**THE DIELECTRIC CONSTANT OF HYDROGEN CHLORIDE FROM
85 TO 165°K.**

BY RICHARD M. CONE, GEORGE H. DENISON AND JACOB D. KEMP

RECEIVED JANUARY 23, 1931

PUBLISHED APRIL 6, 1931

A consideration of the motions of molecules in crystals has led Pauling¹ to conclude that in certain cases there is complete rotation of the molecules at temperatures below the melting point. He also points out that the transition from a condition in which most of the molecules undergo small oscillations about equilibrium orientations, to one in which they rotate completely, may take place over a very small increase of the oscillational quantum number.

Transitions in the solid hydrogen halides involving the absorption of considerable amounts of heat have been reported by Eucken and Karwat² and measured accurately by Giauque and Wiebe.³ The transition in hydrogen chloride^{3a} is perfectly isothermal at 98.36°K., and requires 284.3 calories per mole. Pauling associates such transitions with the taking up of rotational energy.

Whenever the molecules of highly polar substances, such as the hydrogen halides, are free to rotate, those substances must have a high dielectric constant. If the transition in hydrogen chloride at 98.36°K. has produced free rotation of the molecules, then the dielectric constant of the solid should increase considerably at that temperature, in accordance with Pauling's prediction. The purpose of this work was to determine whether or not such an increase occurs.

Apparatus and Experimental Procedure

Hydrogen chloride, prepared by allowing c. p. concentrated sulfuric acid to drop on c. p. sodium chloride, was condensed by liquid air. After

¹ L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

² Eucken and Karwat, *Z. physik. Chem.*, **112**, 467 (1924); Karwat, *ibid.*, **112**, 486 (1924).

³ Giauque and Wiebe, (a) *THIS JOURNAL*, **50**, 101 (1928); (b) *ibid.*, **50**, 2193 (1928); (c) *ibid.*, **51**, 1441 (1929).