

[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

Reactions of Beryllium Chloride. Normal and Basic Organic Salts of Beryllium<sup>1</sup>BY GEO. B. FEILD<sup>2</sup>

Recent work in this Laboratory has led to an improved method for preparing anhydrous beryllium chloride and a study of the reactions of this compound has been undertaken. In the course of an investigation of the catalytic action of anhydrous beryllium chloride<sup>3</sup> in certain types of Friedel-Crafts reactions it was found that organic acid anhydrides react vigorously with this salt to produce beryllium salts of the acid and the corresponding acyl halide.

Anhydrous beryllium chloride also reacts smoothly with various organic acids to yield hydrogen chloride and the normal beryllium salt. Funk and Römer<sup>4</sup> recently have reported the reaction of formic and acetic acids with anhydrous beryllium chloride.

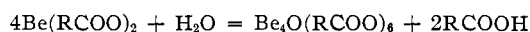
Although there is a fairly extensive literature on the organic salts of beryllium it cannot be reviewed in detail here, but it may be pointed out that previously the various salts have nearly always been prepared by the action of aqueous acid solutions upon beryllium carbonate or hydroxide.<sup>5-9</sup>

The proposed formulas for these salts usually have been calculated from the beryllium content alone. Some investigators have preferred to regard these substances as mixtures or solid solutions of the products of hydrolysis<sup>10</sup> rather than as definite compounds. On the other hand, there are a number of definite organo-beryllium compounds<sup>11-13</sup> to which rational constitutional and even configurational formulas have been assigned. In terms of the newer ideas of valence these com-

pounds, and probably also the so-called basic beryllium salts, are covalent compounds in which beryllium is quadricovalent.<sup>14</sup> For example, the X-ray examination of basic beryllium acetate, presumably  $\text{Be}_4\text{O}(\text{CH}_3\text{CO}_2)_6$ , suggests a tetrahedral distribution of the valence bonds of beryllium.<sup>15</sup>

In view of the situation it was felt that the above methods for preparing the beryllium salts from beryllium chloride should be especially interesting and valuable. The point of greatest importance, aside from the convenience of the procedure, appeared to be the possibility of working in the complete absence of water. This suggested that it might be possible to obtain exclusively the normal salts, since hydrolysis could presumably be avoided. Subsequent experiments confirmed this expectation.

For the preparation of normal salts from organic acids careful preliminary drying is necessary, since only one-fourth mole equivalent of water is sufficient for the complete hydrolysis of the normal to the basic salt.



In a special experiment 5.0 g. of normal beryllium acetate, prepared in the presence of dry benzene, remained as a stable, insoluble solid during prolonged refluxing. When the calculated amount of water (0.035 g.) was added the normal salt rapidly dissolved and the basic acetate crystallized from the mixture on cooling. For this reason it was found necessary to use an all-glass apparatus in which the initial reaction and subsequent purification of the product could be carried out without contamination from cork or rubber connections or from atmospheric moisture. It was also necessary to avoid excessive heating, inasmuch as in earlier experiments attempts to free the normal salt from excess reagents or solvent by heating *in vacuo*, either with a small flame or on an oil-bath, resulted in partial decomposition. The remainder of the product (75-80%) was always the basic salt. It is probable that the decomposition produced enough water to hydrolyze the remaining normal salt.

(14) Sidgwick, "Electronic Theory of Valence," Oxford Press, London, 1932, p. 255.

(15) Bragg and Morgan, *Proc. Roy. Soc. (London)*, **A104**, 437 (1923).

(1) Constructed from a thesis submitted by Geo. B. Feild in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Vanderbilt University. Original manuscript received February 10, 1939.

(2) Present address: Mellon Institute, Pittsburgh, Penna.

(3) (a) Lebeau, *Ann. chim. phys.*, [7] **16**, 457 (1899); (b) Grosse and Ipatieff, *J. Org. Chem.*, **1**, 559 (1937).

(4) Funk and Römer, *Z. anorg. allgem. Chem.*, **239**, 288 (1938).

(5) (a) Tanatar and Kurowski, *J. Russ. Phys.-Chem. Soc.*, **39**, 936 (1907); (b) Tanatar, *Ber.*, **43**, 1230 (1910).

(6) Steinmetz, *Z. anorg. Chem.*, **54**, 217 (1907).

(7) Glassmann, *Chem. Ztg.*, **31**, 8 (1907).

(8) Tanatar and Kurowski, *J. Chem. Soc.*, **94**, 166 (1907).

(9) Lacombe, *Compt. rend.*, **134**, 772 (1902).

(10) (a) Parsons, *J. Phys. Chem.*, **11**, 659 (1907); (b) Parsons, "The Chemistry and Literature of Beryllium," Chem. Pub. Co., Easton, Penna., 1908, pp. 17, 40.

(11) Mills and Gotts, *J. Chem. Soc.*, 3121 (1926).

(12) Booth and Pierce, *J. Phys. Chem.*, **37**, 59 (1933).

(13) Parsons, *THIS JOURNAL*, **26**, 732 (1904).

Using the indicated precautions it was possible to prepare the normal salts from formic, acetic, propionic, benzoic, and *o*-chlorobenzoic acids as well as from acetic, propionic and benzoic anhydrides. The normal salts were all microcrystalline solids, insoluble in benzene and similar solvents, but soluble with decomposition in water, dilute acids and alkalies, and in most polar solvents. The composition was determined by analysis for beryllium, or in some cases by combustion, and agreed closely with the formula  $\text{Be}(\text{RCOO})_2$ .

The pure normal *n*-butyrate was not obtained from either the acid or the anhydride in spite of rigorous drying or various modifications of the procedure. With the latter reagent *n*-butyryl chloride was formed in high yields, as usual, but the crude salt was always waxy or semi-liquid. Unlike the other salts it formed an emulsion with benzene or ligroin, and could neither be crystallized nor completely freed of solvent. Distillation produced partial decomposition and the liquid distillate was identified as the basic salt by its properties and by analysis.

Most of the basic salts were first obtained as by-products during the earlier attempts to prepare the normal salts. When desired they were later prepared by carrying out the reaction with reagents of ordinary grade or by the deliberate introduction of moisture. All of the basic salts were obtained pure except the formate. Addition of the calculated amount of water to the pure normal formate did not cause the usual smooth conversion to the basic salt. However, the normal formate dissolved readily in excess water and the solution then gave a glass on evaporation. The other basic salts, except the butyrate, crystallized from benzene. They are readily soluble in most organic solvents but insoluble in water or dilute acids or alkalies. The solids melted sharply and could be sublimed without serious decomposition. The analyses agreed closely with the formula  $\text{Be}_4\text{O}(\text{RCOO})_6$ .

From these results it is believed that previous attempts to prepare normal beryllium salts usually have failed because of the presence of water and that the new methods afford a convenient and reliable process for obtaining either the normal or basic salts, as desired, at least from simple monobasic acids. The results herein reported have been supplemented by small scale reactions of beryllium chloride with numerous other repre-

sentative monobasic acids of various types. It was noted that all of the reactions followed the usual pattern and the products formed possessed the general properties of the basic beryllium salts. This reaction is therefore probably quite general.

In the latter connection it should be mentioned that beryllium chloride has been observed to react, usually vigorously, with practically every class of organic compounds in which active hydrogen atoms are present. Hydrogen chloride is evolved and the other product as a rule has the general properties of covalent compounds. With the exception of the reactions with acids this behavior of beryllium chloride is not reported in the literature. Although the "solubility" of beryllium chloride in ethyl alcohol and acetone has been reported, no mention is made of the fact that a chemical reaction occurs,<sup>16,17</sup> and no description of the products of these reactions has been given. Apparently the difficulty of obtaining anhydrous beryllium chloride has been partially responsible for the neglect of this promising field. With this reagent now more available a more detailed study of some of these reactions has been undertaken with the hope that they may yield a variety of organo-beryllium compounds not readily accessible by other methods. It is hoped that results of this work will be reported at a later date.

The author wishes to express his indebtedness to Prof. J. M. Breckenridge for direction and to Prof. A. W. Ingersoll for advice.

### Experimental

**Preparation of Beryllium Chloride.**—Beryllium chloride is perhaps most easily prepared by heating the beryllium oxide in a stream of phosgene,<sup>18</sup> but the handling of this latter reagent involves numerous difficulties and hazards. An improvement of the method of Rose<sup>19</sup> was therefore used. This involves heating beryllium oxide with carbon in a stream of chlorine. Since adequate directions for this method of preparing beryllium chloride could not be found in the literature, the improved method may be described in some detail.

Beryllium oxide was prepared from the nitrate (Pfaltz and Bauer, Inc.) by precipitation of the hydroxide with ammonium hydroxide and ignition. This was then mixed with carbon as follows. Five hundred grams of sucrose and 50 g. of the oxide, previously ground to 200-mesh, were heated with stirring in a large evaporating dish until a viscous sirup was obtained. This was then ignited

(16) Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., Vol. IV, 1930, p. 231.

(17) Parsons, "The Chemistry and Literature of Beryllium," Chemical Publishing Co., Easton, Penna., 1908, p. 20.

(18) Booth and Toorey, *J. Phys. Chem.*, **35**, 2465 (1931).

(19) Rose, *Pogg. Ann.*, **9**, 39 (1827).

and allowed to burn without further application of heat. By this means practically all volatile matter was burned off, leaving a very intimate but porous mixture of the oxide and carbon. This was crushed with care to avoid forming much fine powder.

One-third of the oxide-carbon mixture (about 16.7 g. of BeO) was then poured, without packing, into the 500-cc. Pyrex glass reaction chamber (B) of the apparatus shown in Fig. 1. The lower arm of the reaction chamber was previously closed by a loose plug of glass wool near the bulb. The train was then disconnected at the ground-glass joint (K) and the opening into the 1-liter flask (C) temporarily closed with a stopper to prevent the entrance of moisture. To facilitate connection or disconnection at K without disturbance of other connections, the entire train to the right of K was mounted on rollers. Parts of the apparatus rested upon rubber mats (G) to minimize strains. The electric furnace (J) was then slowly heated and the burners under the preheater (A) were lighted. A slow stream of nitrogen was passed through the reaction chamber and continued until the apparatus and charge were thoroughly dried. Toward the end of this process the burner at K was lighted to expel moisture at that point. The heating was so adjusted that when the apparatus was free from moisture the temperature in the preheater and furnace was about 550° or just below the softening point of Pyrex glass. This temperature was then maintained.

The movable part of the train was connected at K and the passage of chlorine, mixed with about an equal volume of nitrogen, was begun. The nitrogen was necessary to offset the decrease in volume that accompanies the reaction and to assist in removing the beryllium chloride from the reaction zone. The use of additional chlorine for this purpose is wasteful and the exit gas is objectionable from the standpoint of disposal. It also should be explained that preheating the gases permitted running the reaction at about 550°. Without preheating, a furnace temperature of about 650–700° was necessary. Use of the preheater therefore made it possible to construct the entire apparatus from Pyrex glass and thus minimize breakage due to uneven expansion of joints. The preheater was loosely filled with broken plate or Pyrex chips and was shielded by a gauze or iron pipe.

At the indicated temperature the reaction occurred readily and the beryllium chloride passed from the reactor as a smoke. The greater part settled in the exit tube and flask C. The tube was heated intermittently at K and sometimes at C and D to prevent clogging. When the stream of nitrogen was properly adjusted, about 95% of the product collected in C, about 4% in D and the greater portion of the remainder in E. Some smoke passed into the trap but the loss was found to be negligible. A charge of the size indicated could be run in about eighteen hours (two nine-hour periods) without significant loss, or in a much shorter time if some loss were permitted or more collection chambers were used. The product collecting in C could be transferred to F and removed occasionally. For this purpose C was heated gently with a large soft flame while being shielded from drafts. The product collecting in D and beyond was usually allowed to accumulate during several runs. The

product was transferred and stored with minimum exposure to air.

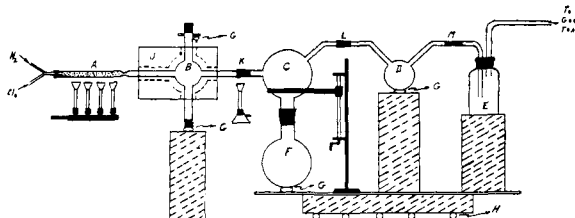


Fig. 1.

The yield of beryllium chloride was 32–37 g. in various runs. Based on the oxide taken, this is 60–70% conversion. The remaining oxide probably escaped conversion because of the removal of all carbon in direct contact with it. The spent charge was removed by withdrawing the glass wool plug from the lower limb of the reaction chamber and was then ignited to recover the oxide. This appeared to contain some non-volatile oxychlorides but was quite suitable for use in preparing another charge. In a series of runs the conversion of the oxide to the chloride was therefore practically quantitative.

In a series of preliminary experiments attempts were made to prepare beryllium chloride from the mixture of iron, aluminum and beryllium oxides obtained from beryl. Although the sublimation points of the corresponding chlorides are reported as 177.8, 315 and 475°, respectively, no appreciable separation could be effected by fractional sublimation. For this reason, commercial beryllium salts as well as the oxide, were unsuitable for the present work.

**Preparation of Organic Salts. (a) Materials.**—The anhydrides were purified by distilling c. p. reagents and collecting the appropriate fraction. Formic acid was prepared by treating the 99% material with phosphorus pentoxide and distillation, with rejection of the forerun. The liquid acids were refluxed with a small amount of the corresponding anhydrides and distilled. The solid acids were recrystallized and dried in a desiccator. Benzene, toluene and ligroin were dried with magnesium perchlorate and distilled.

**(b) Procedure.**—This already has been outlined briefly. In the preparation of normal salts by the use of organic acids, an all-glass apparatus constructed as follows was used. A 250-cc. round-bottomed flask was fitted with a separatory funnel and a side-arm distilling column. A water jacket was fitted into the distilling column, thus enabling refluxing or distillation at will without dismantling. All connections were made by means of ground glass joints. A weighed quantity of the powdered chloride was placed in the flask. The equivalent amount or a slight excess of the acid dissolved in about 5 parts of dry benzene or toluene was then admitted through the separatory funnel. When the initial reaction subsided the mixture was refluxed gently for about one hour, and was then distilled on a water-bath. A little fresh diluent was admitted and the distillation repeated. Analysis of the distillate accounted for approximately the theoretical amount of hydrogen chloride. The residual salt was washed repeatedly with dry benzene and ligroin (b. p. 30–60°), filtered by suction and dried *in vacuo* at room temperature or on a steam-bath. This procedure removed any excess acid and any

TABLE I

Beryllium salt	Class	Form	M. p., °C.	% BeO		Notes
				Found	Calcd.	
Formate	Normal	Micro-cryst.	d. 150	25.12	25.37	<i>b, g</i>
	Basic	Glassy	.....	...	...	<i>b</i>
Acetate	Normal	Micro-cryst.	d. 294-296	19.78	19.68	<i>c</i>
	Basic	Tetrahedral	283-284	24.54	24.64	<i>d, g</i>
Propionate	Normal	Micro-cryst.	d. 75-78	16.73	16.13	<i>b</i>
	Basic	Monoclinic prismatic	133-134	20.01	20.18	<i>e</i>
Butyrate	Normal	Impure	.....	...	...	<i>a</i>
	Basic	Liquid	b. 225, 25 mm.	17.78	17.41	<i>e</i>
Benzoate	Normal	Micro-cryst.	d. 307-309	10.34	9.97	<i>a</i>
	Basic	Pinacoidal triclinic	317-318	13.04	12.85	<i>a, f</i>
<i>o</i> -Chlorobenzoate	Normal	Micro-cryst.	d. 245-249	7.78	7.81	<i>a</i>
	Basic	Prisms	255-256	10.05	10.15	<i>a</i>

<sup>a</sup> Not mentioned in the literature. <sup>b</sup> Tanatar and Kurowski, ref. 5. Disclaimed by Parsons, ref. 10. <sup>c</sup> Steinmetz, ref. 6. <sup>d</sup> Glassmann, ref. 7, and Steinmetz, ref. 6. <sup>e</sup> Impure product by Lacombe, ref. 9. Pure salt by Morgan and Bragg, ref. 15. <sup>f</sup> Amorphous product by Tanatar and Kurowski, ref. 8. <sup>g</sup> Funk and Römer, ref. 4.

basic salt. The normal salts were stable during brief exposure to moist air, but on prolonged exposure gave the odor of the corresponding acid and changed to the basic salt.

A similar procedure was used with acid anhydrides, except that the volatile acyl chlorides distilled with the benzene or toluene while benzoyl chloride was recovered from the filtered washings. In semi-quantitative experiments the acyl halides were isolated in 60-80% yields by fractional distillation and were identified by their boiling points or by conversion to anilides.

Reactions were also carried out with a large excess of the liquid acids or anhydrides in the absence of benzene but the procedure was less satisfactory because of the difficulty of removing the excess reagent.

Most of the basic salts were first prepared as by-products in preliminary experiments in which anhydrous conditions were not maintained. Alternatively, the procedure for forming the normal salts was followed and then moist benzene was added. The mixture was refluxed until the product dissolved. The hot filtered solution deposited the basic salt on cooling. Basic beryllium acetate could also be crystallized from acetic acid.

(c) **Analyses.**—The salts were dissolved in hot, concentrated nitric acid. For the basic salts it usually was necessary to reflux for a few minutes to complete the decomposition and in this case care was taken that none of the material was lost by volatilization. The solution was

then diluted and the beryllium was precipitated as hydroxide with excess ammonium hydroxide and ignited to the oxide. In the case of the benzoates and *o*-chlorobenzoates the partially nitrated acid appeared on dilution but dissolved in an excess of ammonia. Although calculated values of BeO were obtained in this way, these analyses were also confirmed in some cases by combustion, using the method of Fieser.<sup>20</sup> The properties and analyses are recorded in the table.

### Summary

1. A convenient procedure for the preparation of anhydrous beryllium chloride is described.
2. A new method is described for the preparation of beryllium salts by means of the reactions of anhydrous beryllium chloride with organic acids or acid anhydrides.
3. Normal beryllium formate, acetate, propionate, benzoate, and *o*-chlorobenzoate and also basic beryllium acetate, propionate, *n*-butyrate, benzoate and *o*-chlorobenzoate were prepared and analyzed.

NASHVILLE, TENNESSEE

RECEIVED MAY 19, 1939

(20) Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., New York, N. Y., 1925, p. 350.