essentially confirmed those above, showing a small margin in favor of the electrical distillation.

Because a single experiment is never conclusive, it was thought worth while to repeat the comparison, in this case taking the temperatures at intervals of two minutes throughout each distillation. The volumes also at each of these intervals were measured, but need not be detailed here. The distillation was carried out essentially as before, care being taken that the conditions should be essentially similar in the two cases. In this case the two were not carried out simultaneously, however; and it happened that the pressure during the electrical distillation was 5 mm. less than in the ordinary distillation, and the rate of distillation was slightly greater in the latter case. The difference is so slight, however, that it could hardly have had any essential effect upon the results.

SECOND COMPARISON OF METHODS OF DISTILLATION.

	Ordinary distillation.			Electrical distillation.		
Fraction.	Range of boiling point.	Density.	Per cent. of alcohol.	Range of boiling point.	Density.	Per cent. of alcohol.
I.........	80– 83°	0.8445	84.0	78–80.5°	0.8404	85.2
II.........	83– 98°	0.8934	65.5	80.5–98°	0.8899	66.9
III.........	98–100°	..	..	....	..	..

These results agree essentially with the previous ones, giving a verdict slightly in favor of electrical distillation.

The range of temperature in the first fraction was somewhat less when the distillation was conducted electrically than when the vessel was heated from outside, but the gain in purity, as indicated in the preceding table, was not quite great enough to correspond to this diminished temperature range. The superheating evidently at first amounted to about 1.8° in the case of the ordinary distillation, but was negligible in the electrically conducted process.

In brief, this note shows that while distillation by means of a wire heated electrically effects a somewhat better separation than the ordinary method and causes much less superheating in the liquid, the gain in the efficiency of separation is not always as great as had been at first inferred from the great constancy of boiling point observed in a special series of cases.

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SOME ORGANIC COMPOUNDS OF BERYLLIUM.

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It has been repeatedly pointed out by one of us[1] that solutions of the

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[1] THIS JOURNAL, **26**, 1444; **28**, 555. *Z. anorg. Chem.*, **49**, 178. *J. Physic. Chem.*, **11**, 651. "Chemistry and Literature of Beryllium," p. 61.

normal salts of beryllium have, without exception, the power of dissolving a large excess of beryllium when treated with beryllium hydroxide or carbonate, that the extent of this solution increases with the concentration, and that highly basic solutions result which, on evaporation, give gummy masses which are sometimes crystalline in appearance but never so in fact. An explanation of this phenomenon has been offered,[1] and the general claim has been made that no true compound of beryllium of definite composition will probably ever be made by *saturating* an acid with beryllium hydroxide or carbonate and certainly not in aqueous solution. It was, accordingly, a distinct surprise to us to note that both Glassmann and Tanatar and Kurovskii have recently claimed to make in this manner definite beryllium compounds of many organic acids. The facts that their so-called compounds were based, in most instances, solely upon the beryllium oxide content of residues of evaporation which passed through a gummy consistency to a glassy or apparently crystalline mass; that their cryoscopic evidence when obtained is valueless because beryllium hydroxide dissolved in solutions of its normal salts *raises* the freezing point;[2] and that Glassmann was obliged to assume more or less hydration for his new salts in order to satisfy the typical formulas assumed by him from the meager data of the beryllia content led us to doubt the accuracy of their conclusions and to study again this question.

Glassmann, as well as Tanatar and Kurovskii, has studied many organic compounds in their controversy as to whether beryllium is bivalent or quadrivalent. We question only those which were prepared in the presence of water by saturating with beryllium hydroxide or carbonate unless enumerated below. Those claimed by Glassman which come under this head are: Picrates, $Be(C_6H_2O_7N_3)_2.3H_2O$ and $Be(C_6H_2O_7N_3)_2$-$20Be(OH)_2$;[3] lactate, $Be_2O(C_3H_5O_3)_2.H_2O$; glycolate, $Be_2O(C_2H_3O_3)_2.H_2O$; trichloracetate, $Be_2O(C_2Cl_3O_2)_2$; ethylglycolate, $Be_2O(C_2H_5.C_2H_2O_3)_2.H_2O$; phenylglycolate, $Be_2O(C_6H_5.C_2H_2O_3)_2$; chloropropionate, $Be_2O(C_3H_4ClO_2)_2.H_2O$; salicylate, $Be_2O(C_7H_5O_3)_2$; cyanacetate, $Be_4O(C_2H_2CNO_2)_6$; dichloracetate, $Be_4O(C_2HCl_2O_2)_6$; monochloracetate, $Be_4O(C_2H_2ClO_2)_6$; monobromacetate, $Be_4O(C_2H_2BrO_2)_6$; monobromopropionate, $Be_4O(C_3H_4BrO_2)_6$.[4] All of those prepared by Glassmann with the exception of his picrate, prepared earlier, come under typical forms $Be_4O(R)_6$ or $Be_2O(R)_2$. Tanatar and Kurovskii, on the other hand, had been arguing for the quadrivalency of beryllium and the organic compounds produced by them[5] were assigned very different formulas for the bivalent acids.

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[1] *J. Physic. Chem.*, **11**, 659.

[2] *Ibid.*, **11**, 658.

[3] *Ber.*, **40**, 3159.

[4] *Ibid.*, **41**, 33.

[5] *J. Russ. Phys. Chem. Soc.*, **39**, 936, 1630; **40**, 787.

They claimed the formates $Be(CHO_2)_2$ and $Be_4O(CHO_2)_6$, entirely distinct in their properties and preparation from the true formate, $Be_4O(CHO_2)_6$, prepared by Lacombe;[1] crotonate, $Be_4O(C_4H_5O_2)_6$; isocrotonate, $Be_4O(C_4H_5O_2)_6$; levulinate, $Be_4O(C_5H_7O_3)_6$; succinate, $Be_4O(C_4H_4O_4)_3$; maleate, $BeC_4H_2O_4$; fumarate, $BeC_4H_2O_4$; citraconate, $BeC_5H_4O_4$; tricarballyllate, $Be_3(C_6H_5O_6)_2$; citrate, $Be_5O_2(R)_2$; phthalate, $Be_5O_2(R)_2$; salicylate, $Be_3O_2(R)_2$; lactate, $Be_3O_2(R)_2$; benzoates, $Be_{10}O_9(R)_{22}$ and $Be_4O(R)_6$. Also Tanatar and Kurovskii in their latest communication[2] state that several other salts of benzoic acid were produced, varying with the temperature, concentration, etc., but they apparently do not recognize that they were doubtless all solid solutions and not compounds at all and that the other acids named would also yield variable products under like treatment. It should also be noted that the investigators named do not agree as to the formula of salts of lactic or salicylic acids, which are the only ones studied in common.

Of the salts enumerated above the only one in our opinion that can be produced in the presence of water is the trichloracetate and possibly the dichloracetate. The former, however, has a very different formula from that ascribed to it by Glassmann and requires excess of acid in its water solution if it is to be crystallized therefrom and kept from hydrolysis.

In studying this problem we have worked with the following acids, succinic, lactic, glycollic, salicylic, citric, phthalic, benzoic, picric, monochloracetic and trichloracetic. We have used many other solvents than water, have used aqueous solutions of various concentrations, have saturated these at various temperatures and have attempted to crystallize possible compounds both from solutions containing beryllium in excess of the hydrogen equivalent and from solutions containing excess of acid. Only the highly ionized trichloracetic acid has yielded anything that could be identified as a compound and this acted exactly like all other acids when any attempt was made to saturate it with beryllium carbonate. Such saturation is difficult, even if possible, to attain and the solutions so produced on evaporation *separate* no solid but pass through various stages of viscosity to gummy and finally glassy residues. If washed with alcohol or other non-aqueous solvent the residues may become finely granular and crystalline in appearance, but careful examination under the microscope fails to show any true crystals. The composition of the residues depends simply upon the amount of acid present and the amount of beryllium carbonate dissolved, while this latter depends upon the concentration of the acid. The ease of solution depends upon the temperature. In most cases the *limit of saturation* was near to that found on analysis by the investigators already mentioned. If,

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[1] *Compt. rend.*, 139, 772.

[2] *J. Russ. Phys. Chem. Soc.*, 40, 787

however, highly concentrated solutions of some of these acids were used the solutions became thick, viscous and even semi-solid some time before the limit of saturation was reached and on diluting those solutions a white flocculent precipitate of beryllium hydroxide, occluding some of the acid, was thrown out. Dilute solutions of the acids simply held proportionately less beryllium in solution, although all became basic from the standpoint of the hydrogen equivalent. All these acids acted perfectly analogous to the sulphates and oxalates[1] except that only with the trichloracetate could a high enough concentration of hydrogen ions be secured to insure the separation of the normal salt.

Many combustion analyses of the products obtained by us were made as well as determining the simple beryllia content of others. To print them here would be a waste of space as the beryllium content was simply a record of the amount dissolved and the ratio of base to acid in the residues increased with the concentration of the acid used. We succeeded in getting a higher ratio of base dissolved in acid than either of the investigators mentioned even in the cases of the lactate and salicylate where Tanatar and Kurovskii obtained a much more basic residue than Glassmann. In the case of the benzoate obtained by Tanatar and Kurovskii,[2] the crystalline precipitate thrown out on adding a solution of beryllium carbonate in *excess* of acetic acid to sodium benzoate was simply benzoic acid occluding more or less beryllium. Acetic acid itself gave a perfectly similar precipitate, containing, however, no beryllium, and unless an excess of acid was present no precipitate appeared.

The residues obtained from any acid or degree of saturation were much alike in physical properties, such as appearance, solubility in solvents, etc., although varying greatly in basicity.

Beryllium Trichloracetate.

Although the trichloracetate claimed by Glassmann as having the formula $Be_2O(C_2Cl_3O_2)_2$ is simply the result of analysis of an indefinite residue of evaporation, the true compound, which he did not make, is easily produced when the properties of beryllium are understood. It has the formula $Be(C_2Cl_3O_2)_2 + 2H_2O$ or that of the normal salt. The only precaution necessary for its preparation is that the trichloracetic acid shall be present in *excess* of the amount required by the formula. On evaporating such a solution the salt crystallizes out together with the acid itself, which has about the same solubility. There is no viscous residue produced and under the microscope the two forms of crystals can be distinguished. The salt obtained is the same in all cases whether much or no water is present. It

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[1] "Chemistry and Literature of Beryllium," pp. 65 and 66. THIS JOURNAL, 26, 1444; 28, 555. *J. Physic. Chem.*, 11, 655.

[2] *Loc. cit.*

can be separated from the trichloracetic acid by washing out the latter with chloroform, carbon tetrachloride, carbon disulphide, benzene, nitrobenzene or toluene in which the salt itself is nearly insoluble. Chloroform is on the whole the best liquid to use for the purpose. Once separated from trichloracetic acid (as hydrolysis takes place it cannot be crystallized from water), some acid is lost and the residue comes down in the characteristic gummy form of the basic residues previously described. A slight excess of trichloracetic acid allows it to crystallize again.

Its constancy of composition is shown by the two following analyses:

1st. By adding basic beryllium carbonate to a dilute solution of trichloracetic acid, evaporating over sulphuric acid, and washing with chloroform. BeO 6.80, Cl 57.55 per cent.

2nd. By dissolving basic beryllium carbonate in excess of fused trichloracetic acid and washing with chloroform. BeO 6.79, Cl 57.48 per cent. $Be(C_2Cl_3O_2).2H_2O$ requires BeO 6.79, Cl 57.51 per cent.

The product in both cases was identical in crystalline form and chemical and physical properties.

Beryllium trichloracetate is soluble in water, ethyl, methyl and amyl alcohol, acetone, ether and ethyl acetate. In pyridine it first forms a thick, jelly-like mass, which is soluble in excess. In a water bath at 97° it loses most of its water of hydration and also a little trichloracetic acid passes away therewith, as would be expected from the known properties of other salts of beryllium. Heated somewhat higher it decomposes, yielding beryllium chloride, which volatilizes except that portion converted to oxide by the hydrolytic action of any water present.

Summary.

Organic acids form no exception to the rule that true basic compounds of beryllium cannot be made in the presence of water and that the residues of evaporation of such basic solutions as described herein are but indefinite mixtures or solid solutions.

Beryllium trichloracetate is a definite compound of the composition $Be(C_2Cl_3O_2)_2.2H_2O$, produced only in the presence of an excess of trichloracetic acid.

Normal compounds of beryllium with acids having a much lower ionization constant than oxalic acid have not been made and it is improbable that a high enough concentration of hydrogen ions can be obtained to allow them to separate as distinct individuals from aqueous solution.

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