3. With Water and Alcohol.

Phenylbromomethylbenzoate gradually dissolved in ethyl alcohol After standing a day, the solution was distilled *in vacuo* and benzaldehyde and ethyl benzoate were obtained as the main products, although some unidentified halogen compounds were present in small amounts.

The instability of many of these addition compounds in air has already been mentioned. This is undoubtedly due to the presence of moisture present in the air. The stability in water varies in same way as the stability in air. All will subsequently decompose to give benzoic acid, halogen acid, and benzaldehyde.

Summary.

1. The reaction between aromatic aldehydes and aromatic acid halides seems to be a general one.

(*a*) Benzoyl bromide, (*b*) benzoyl chloride and a number of its substitution products, (*c*) oxalyl bromide have been condensed with various aromatic aldehydes.

2. The substances formed are addition compounds of one molecule of acid halide and one molecule of aldehyde (in the case of oxalyl bromide, one molecule of acid halide to two of aldehyde).

3. The constitution of the substances is represented by the general formula RCHXOCOR (or RCHXOCOCOOCHXR if oxalyl halides are used).

4. These compounds have been treated with water, alcohol, ammonia, certain amines and silver salts of organic acids. In some cases the reactions are those to be expected from a mere mixture of acid halide and aldehyde, in other cases are characteristic of these substances.

URBANA, ILL.

ZIRCONYL BASIC BENZOATES AND SALICYLATES.

BY F. P. VENABLE AND F. R. BLAYLOCK.

Received September 17, 1918.

Nothing definite has appeared in the literature as to the composition of compounds of zirconium and benzoic or salicylic acids. The formation of certain precipitates only has been mentioned by Mandl.[1] Rosenheim and Hertzman[2] have, by the action of benzoic acid upon zirconium tetrachloride in ether solution, prepared a compound $ZrCl_2(C_6H_5.CO_2)_2$. We have subjected these basic salts to examination, so far as time allowed, with the following results: It may be stated that the chief interest attaches to the general behavior of zirconium, or rather the radical zirconyl, toward organic acids, which has been only imperfectly studied. Apologies should be offered for the incompleteness of this present study. It has

---

[1] *Z. anorg. Chem.*, **37**, 252 (1903).

[2] *Ber.*, 40, 812 (1907).

been cut short by the exigencies of the war and the various phases of the investigation opening up as the work progressed could not be followed up.

Benzoates.

Preparation.—Upon the addition of a cold saturated solution of benzoic acid to an acid or neutral solution of zirconyl chloride a white cloud appeared and a fine, white, granular precipitate slowly settled out. This was difficult to filter on account of its fine subdivision. On mixing the solutions heated to boiling a white, gelatinous precipitate formed, which settled easily and could be readily washed and filtered. Both varieties of precipitates dissolve in ammonium hydroxide. For the following experiments the precipitation was carried out with hot solutions and washed with hot water: After washing, the precipitate was tested for chlorine and found to be free from it. This precipitate could be dried to a fairly constant weight at 100° but continued to lose weight if heated beyond that temperature. Evidences of charring were observed on heating it above 300°. The precipitates also steadily lost weight when placed in a desiccator over calcium chloride. Preparations dried between filter paper and afterwards in air were used for analysis, duplicate samples being taken simultaneously for the complete analysis to secure concordant results irrespective of the water present.

Analysis.—For the zirconium the sample was ignited to a constant weight and weighed as zirconia. It is known, of course, that such results tend to be too low on account of the carrying off of the finely divided oxide. For the benzoic acid the carbon was determined by the usual combustion method and the percentage of the acid calculated. Under the circumstances duplicate analyses for the acid radical gave only fair results. Closer accord, however, was not necessary in order to settle the composition of the compound. Three preparations were analyzed. The duplicate analyses gave:

No. 1.—Calc. for $ZrO(OH)_2.2ZrO(C_7H_5O_2)_2.6H_2O$: Zr, 28.99; $C_7H_5O_2$, 50.99. Calc. for $Zr_3(OH)_8.(C_7H_5O_2)_4.4H_2O$: Zr, 28.45; $C_7H_5O_2$, 50.03. Found: Zr, 29.07; $C_7H_5O_2$ (mean), 49.21; C, 34.52, 34.42; $C_7H_5O_2$, 49.33, 49.09.

No. 2.—Calc. for $ZrO(OH)_2.6ZrO(C_7H_5O_2)_2.6H_2O$: Zr, 27.64; $C_7H_5O_2$, 61.09. Found: Zr, 27.59; $C_7H_5O_2$, 59.90 (only one analysis made).

No. 3.—Calc. for $ZrO(OH)_2.3ZrO(C_7H_5O_2)_2.16H_2O$: Zr, 24.81; $C_7H_5O_2$, 49.01. Found: Zr, 24.62; $C_7H_5O_2$ (mean), 49.11; C, 34.01, 34.10; $C_7H_5O_2$, 49.00, 49.22.

The deduction to be drawn seems to be that under varying conditions as to concentration, etc., no single definite compound is formed. Instead of that, precipitates are obtained with varying ratios between the acid radical and the partly dehydrated zirconium hydroxide, showing an undetermined capacity in that direction. The water of hydration is perhaps negligible considering the unsurmounted difficulties of drying previous to analysis.

In the case of No. 1 the formula involving the use of zirconium hydroxide is given because of its identity with that assigned by Rosenheim and Frank[1] to a zirconyl tartrate prepared in a similar manner. These authors report that when dissolved in alkali and reprecipitated by acids its composition remained unchanged. We are unwilling to make use of such a formula as that given by Rosenheim and Frank, as it ignores the partial dehydration of zirconium hydroxide in hot water and the formation of a zirconyl hydrate.

Salicylates.

The salicylates were prepared in a manner similar to that used for the benzoates. There is a noteworthy difference in the stability of the precipitates. The salicylates are more easily changed on heating. They turn brown at 100° and become black at 160°. The analyses were carried out as for the benzoates:

No. 1.—Calc. for $2ZrO(OH)_2.3ZrO(C_7H_6O_3)_2.7H_2O$: Zr, 30.06; $C_7H_6O_2$, 54.30. Found: Zr, 29.79; $C_7H_6O_3$ (mean), 54.78, C, 33.55, 33.16; $C_7H_6O_3$, 55.12, 54.43.

No. 2.—Calc. for $2ZrO(OH)_2.3ZrO(C_7H_6O_3)_2.26H_2O$: Zr, 24.60; $C_7H_6O_3$, 44.19. Found: Zr, 25.25; $C_7H_6O_3$ (mean), 44.66; C, 25.89, 26.27; $C_7H_6O_3$, 45.52, 43.15.

No. 3.—Calc. for $2ZrO(OH)_2.3ZrO(C_7H_6O_3)_2.14H_2O$: Zr, 27.88; $C_7H_6O_3$, 50.35. Found: Zr, 27.82; $C_7H_6O_3$ (mean), 49.75; C, 30.50, 30.05; $C_7H_6O_3$, 50.10, 49.41.

The calculations in the case of No. 2 show too great a divergence from the analyses to indicate a closely definite molecular ratio of the two components. Determinations of water in these preparations could not be accurate on account of incipient decomposition. They were approximately, however, in the ratio 1 : 4 : 2 after deducting the amount of water in the zirconyl hydroxide and that formed in the combustion of the salicylic radical. No. 2 is probably to be regarded as impure.

One may be justified in regarding the tendency in the case of the salicylates as being in the direction of forming one basic compound in spite of varying conditions of formation, showing in this a difference from the precipitates formed with benzoic acid.

CHAPEL HILL, N. C.

---

[1] *Ber.*, 40, 803 (1907).