[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Aluminum Acetates and Propionates—Their Preparation and Composition[1]

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Although aluminum acetates have been reported,[2–6] there is variation in the formulas given and even controversy regarding the existence of aluminum triacetate as well as other aluminum trisoaps. During the course of this investigation it was found that the preparation of aluminum salts by aqueous double decomposition reactions between acetates or propionates and aluminum compounds resulted in the formation of disubstituted aluminum salts. In order to prepare aluminum triacetate and tripropionate it was necessary to work under strictly anhydrous conditions. The triacetate was prepared by the method of Lösch.[4] We also found it possible to prepare both the triacetate and tripropionate by refluxing a mixture of the appropriate acid and its anhydride over solid anhydrous aluminum chloride.

Experimental

The composition of the compounds prepared was established by analysis for carbon, hydrogen and aluminum. Aluminum was determined gravimetrically by ignition to the oxide. Carbon and hydrogen were determined by the conventional semimicro procedure. X-Ray diffraction patterns were taken for all of the compounds prepared. These served for quick comparison of compounds prepared by different procedures and to establish the formation of definite compounds. They also gave information as to the crystal size of the compounds. The patterns were taken using nickel-filtered X-rays from a copper target. The exposure time was about four hours with a potential of 37.5 kilovolts and a current of 20 milliamperes.

Aluminum Diacetate $\mathrm{Al(OH)(CH_3CO_2)_2}$.—This compound was prepared by the aqueous double decomposition of 5 g. of sodium acetate and 4.9 g. of aluminum chloride hexahydrate, each dissolved in 25 ml. of water. The sodium acetate used was Mallinckrodt N. F. VII granulated. The salt was recrystallized from water and rendered anhydrous before use. The aluminum chloride hexahydrate was reagent grade and was used without further purification. The white curdy precipitate which formed was filtered, washed with water, and oven-dried at 110°. A yield of 2.8 g. (85%) was obtained.

Anal. Calcd. for $\mathrm{AlC_4H_7O_5}$: Al, 16.64; C, 29.64; H, 4.36. Found: Al, 17.29; C, 29.86; H, 4.39.

The diacetate was also prepared by a method described by Sheĭnkman.[6] Upon treating 3 g. of aluminum hydroxide, prepared by his method, with 16 ml. of 30% acetic acid, a precipitate of 5.1 g. (82%) of aluminum diacetate was obtained.

The diffraction patterns of the aluminum diacetates prepared by both procedures were identical. The interplanar spacings were calculated and appear in Table I.

TABLE I

INTERPLANAR SPACINGS OF ALUMINUM DIACETATE

d	Intensity	*d*	Intensity
8.55	S	2.39	VW
7.05	M	2.32	VW
6.72	S	2.16	VW
5.70	VW	2.10	VW
5.20	VW	2.05	VW
4.90	M	2.00	VW
4.55	M	1.94	VW
4.35	M	1.88	VW
3.91	M	1.81	VW
3.72	VW	1.75	VW
3.51	VW	1.72	VW
3.38	M	1.53	VW
3.17	W	1.46	VW
3.02	W	1.41	VW
2.96	W	1.36	VW
2.70	VW	1.21	VW
2.46	W		

VS, very strong; S, strong; M, medium; W, weak; VW, very weak.

Aluminum Dipropionate $\mathrm{Al(OH)(CH_3CH_2CO_2)_2}$.—This salt was prepared by the aqueous double decomposition of 5 g. of sodium propionate and 4.2 g. of aluminum chloride hexahydrate, each dissolved in 25 ml. of water. The sodium propionate was prepared by the neutralization of propionic acid with sodium hydroxide. It was recrystallized twice from water and thoroughly dried before use. The precipitate was filtered, washed with water, and dried at 110°. A yield of 2.6 g. (79%) was obtained.

Anal. Calcd. for $\mathrm{AlC_6H_{11}O_5}$: Al, 14.18; C, 37.90; H, 5.84. Found: Al, 14.91; C, 38.31; H, 5.90.

The X-ray diffraction pattern of this compound was taken and the calculated interplanar spacings appear in Table II.

TABLE II

INTERPLANAR SPACINGS OF ALUMINUM DIPROPIONATE

d	Intensity	*d*	Intensity
8.70	S	2.82	S
7.94	VS	2.18	VW
7.07	W	2.01	W
5.70	W	1.99	M
4.85	M	1.63	W
4.61	W	1.55	W
4.27	VW	1.43	VW
3.77	M	1.41	VW
3.55	W	1.26	VW
3.28	M	1.15	VW

Aluminum Triacetate $\mathrm{Al(CH_3CO_2)_3}$.—A solution of 20 ml. of glacial acetic acid and 20 ml. of acetic anhydride was refluxed for about half an hour to eliminate any water which might have been present. To this hot solution was added 3 g. of solid anhydrous aluminum chloride which dissolved. As the solution cooled to room temperature a finely divided white precipitate formed. This was filtered, thoroughly washed with dried acetone, and oven-dried at 110°. A yield of 2.9 g. was obtained. The product was kept in a vacuum desiccator over phosphorus pentoxide.

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(1) From a thesis submitted by George C. Hood in partial fulfillment of the requirements for the degree of Master of Science in the University of Wisconsin, 1949.

(2) L. Gmelin, "Handbuch der anorganischen Chemie," No. 35, Part B, Verlag Chemie, Berlin, 1934, p. 295.

(3) G. Spacu and E. Popper, *Kolloid Z.*, **103**, 19 (1943).

(4) J. Lösch, U. S. Patent 2,141,477.

(5) V. R. Gray and A. E. Alexander, *J. Phys. Colloid Chem.*, **53**, 23 (1949).

(6) A. I. Sheĭnkman, *Ukrain. Gosudarst. Inst. Eksptl. Farm (Kharkov) Konsul'tatsionnye Materialy*, 242 (1939); *C. A.*, **36**, 3325 (1942).

The process can also be successfully carried out by adding a saturated solution of aluminum chloride dissolved in nitrobenzene. Anhydrous conditions (including freedom from atmospheric moisture), must be maintained to prevent hydrolysis of the salt.

Anal. Calcd. for $AlC_6H_9O_6$: Al, 13.21; C, 35.30; H, 4.45. Found: Al, 13.94; C, 35.50; H, 4.47.

In verifying the method of Lösch,[4] 3 g. of granular aluminum metal was added to a mixture of 60 g. of acetic acid and 3 g. of acetic anhydride and the solution refluxed. The white precipitate which formed was separated from the remaining aluminum, washed with dried acetone, and dried at 110°. A yield of 9.6 g. was obtained. A greater yield could undoubtedly have been obtained had the reaction been allowed to continue for a longer period.

The diffraction pattern of the aluminum triacetate prepared from aluminum chloride was quite diffuse, indicating very minute sized crystals.[7] A sharp pattern was not obtained until the crystals had been refluxed in acetic anhydride for a half hour. The pattern of the aluminum triacetate prepared by our method was identical with the pattern of the compound prepared according to the procedure of Lösch. The interplanar spacings are recorded in Table III.

TABLE III

INTERPLANAR SPACINGS OF ALUMINUM TRIACETATE

d	Intensity	*d*	Intensity
9.62	S	3.05	VW
8.08	S	2.92	VW
7.86	VS	2.85	VW
6.72	M	2.49	VW
6.23	W	2.39	VW
4.98	W	2.26	VW
4.60	W	2.17	VW
3.98	W	2.11	VW
3.85	M	2.02	VW
3.65	VS	1.89	VW
3.50	W	1.87	VW
3.37	W	1.52	VW
3.17	VW	1.49	VW

Aluminum Tripropionate $Al(CH_3CH_2CO_2)_3$.—To a refluxed mixture of 20 ml. of propionic acid and 20 ml. of propionic anhydride was added 3 g. of solid anhydrous aluminum chloride. Upon cooling, a white precipitate formed which was filtered, washed with dried acetone, and dried at 110°. A yield of 3.4 g. was obtained. The compound was also prepared with the aluminum chloride dissolved in nitrobenzene.

Anal. Calcd. for $AlC_9H_{15}O_6$: Al, 10.95; C, 43.90; H, 6.15. Found: Al, 11.84; C, 44.18; H, 6.24.

It was not found possible to prepare the tripropionate using the procedure suggested by Lösch.

The diffraction pattern of the aluminum tripropionate was also extremely diffuse. The crystals could not be refluxed in propionic anhydride since they were soluble. Hence, dried acetone was employed and a sharp pattern obtained. The interplanar spacings are recorded in Table IV.

TABLE IV

INTERPLANAR SPACINGS OF ALUMINUM TRIPROPIONATE

d	Intensity	*d*	Intensity
8.49	S	3.55	W
8.03	VS	3.27	W
6.67	VW	3.21	VW
6.37	VW	2.85	VW
6.06	VW	2.60	VW
5.53	VW	2.45	VW
5.25	VW	2.37	VW
4.86	M	2.22	VW
4.60	W	1.99	VW
4.27	VW	1.87	VW
3.79	M[a]		

[a] Very diffuse.

Summary

A method of preparation for aluminum diacetate and dipropionate is given along with a verification of Sheĭnkman's procedure for the preparation of the diacetate.

A new method is described for the preparation of aluminum triacetate and tripropionate and Lösch's procedure for the preparation of the triacetate is verified.

The X-ray powder diffraction patterns of the above compounds were taken and the interplanar spacings reported.

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(7) C. W. Bunn, "Chemical Crystallography," Oxford University Press, London, 1948, p. 127.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF SOUTHERN CALIFORNIA]

Surface Areas of Proteins. II. Adsorption of Non-Polar Gases[1]

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In an earlier paper[2] we reported on the initial results of a program of investigation of the surface properties of dry, lyophilized proteins through the methods of gas adsorption. In the present paper we wish to report the additional results which have been obtained through an extension of this work to a study of the adsorption of a series of non-polar gases of different molecular dimensions on dry, lyophilized proteins.

The purpose of the present investigation was to discover whether or not the protein particles contained any appreciable pore structure, by measuring the isotherms of gases of different molecular diameter; and to try to confirm the inherently particle dependent nature of the property of physical adsorption. To accomplish this the following series of non-polar gases was selected: nitrogen, oxygen, argon, methane, neopentane, sulfur hexafluoride and *n*-butane. For purposes of comparison the isotherms were measured for each gas at a set of nearly corresponding temperatures, in the vicinity of their normal boiling points.

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(2) Benson and Ellis, THIS JOURNAL, **70**, 3563 (1948).