CXCV.—*Acid Soaps: A Crystalline Potassium Hydrogen Dioleate.*

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No acid soaps of definite composition have been shown to exist, although the analogous acid sodium acetates ($NaC_2H_3O_2,C_2H_4O_2$, and $NaC_2H_3O_2,2C_2H_4O_2$) have long been known. The present paper describes the preparation of the first definite crystalline compounds of this type observed with the soaps.

Potassium hydrogen dioleate was first prepared from oleic acid "Kahlbaum" and a special Kahlbaum preparation of potassium oleate. These were dissolved in distilled alcohol, and upon cooling with ice a crystalline deposit was obtained. Two or three recrystallisations completely removed any brown colour. The crystals were dried, after being washed with ice-cold alcohol, in a vacuum desiccator over fused calcium chloride for 8—10 days; they then attained constant weight and the analysis was not altered by further drying at 40° in a vacuum.

The acid soap was analysed as follows. To a weighed quantity of solution contained in a stoppered flask a measured excess of standard hydrochloric acid was added slowly from a pipette with vigorous stirring. The precipitated fatty acid was allowed to stand over-night, for the resulting emulsion to clear, and then filtered off through wetted filter-paper and washed free from hydrochloric acid with boiled-out distilled water. The filtrate was titrated with standard sodium hydroxide and phenolphthalein; the difference between this and the amount of hydrochloric acid originally taken determines the total concentration of soap and hydroxide. The fatty acid on the filter paper was dissolved in boiled-out alcohol and titrated with sodium hydroxide, which had been standardised both against the oleic acid used and against hydrochloric acid (Hulett and Bonner, *J. Amer. Chem. Soc.*, 1909, **31**, 345), more boiled-out alcohol being added, if necessary, in order to maintain an alcohol concentration of 70—80%. Determinations of saponification value gave results in good agreement with this method of analysis.

The procedure ultimately adopted was to obtain crystals of acid soap from alcoholic solutions containing various proportions of potassium oleate and oleic acid. The analyses in the table show that the crystals contained one equiv. of oleic acid to one equiv. of potassium oleate, and that the composition over a wide range was independent of the proportions in the alcohol. In each case, 3—4 g. of acid soap were taken for analysis and about 6 g. for saponification values. The amounts of oleate and potassium found by analysis agreed with the total weight of sample taken within 0·2%.

Analysis of crystals obtained from alcoholic solutions of potassium oleate and oleic acid in various proportions.

Propn. in alc.	Ratio in crystal (Oleate/K).	Mol. wt. from saponification value.
KOl : 2HOl.	2·011	—
KOl : HOl.	2·007, (1·952), 1·980, 1·990, 1·986, 2·006, 2·005	600, 600·4
2KOl : HOl.	—	602·6, 601·9
3KOl : HOl.	—	903·1, 905·7
	Theory for KOl : HOl =	602·6
	,, ,, 2KOl : HOl =	923·1

The following method of preparation was found convenient: 130 G. of oleic acid and 145 g. of potassium oleate are dissolved in alcohol by warming, diluted to a litre, and allowed to crystallise at 0°. The white crystals are recrystallised 3 or 4 times—the last time only, from dry alcohol. Drying is completed in a vacuum over frequently-changed fused calcium chloride. This process not only removes the colour, if impure oleic acid is used, but results in definite purification.

The acid soap may be recrystallised from pure oleic acid instead of alcohol; the ratio of oleate to potassium in such a recrystallised product, dried in a screw press with renewed layers of filter paper, was found by analysis to be 2·026 and 2·004.

Potassium hydrogen dioleate forms well-defined crystalline plates; the photograph (Fig. 1) shows a typical group of crystals with dark-ground illumination. This compound possesses a transition point at 43°, at which temperature the solid partly liquefies, and it is only upon heating the system to above 107° that it again becomes homogeneous, giving a clear liquid.

In order to determine whether potassium oleate or a second acid soap was the decomposition product, a quantity of the crystals was placed in a screw press between a number of filter-papers, and kept in an oven at 55—60°, the filter-papers being changed until no more oily liquid was removed from the press cake. Analysis of the product showed that the ratio of oleate radical to potassium was 1·001. Thus the decomposition product at 55° is neutral potassium oleate, the other phase being a liquid solution of potassium oleate in oleic acid.

Further communications will contain the results of phase-rule investigations in the two-component systems soap–fatty acid and the three-component systems soap–fatty acid–water.

Summary.

A definite crystalline compound, anhydrous potassium hydrogen dioleate, has been obtained, showing a transition point at 43° at which it breaks up into potassium oleate and a liquid solution of oleate and oleic acid. It crystallises unaltered from oleic acid or from various compositions of alcoholic solution. It offers a means of purification of oleic acid.

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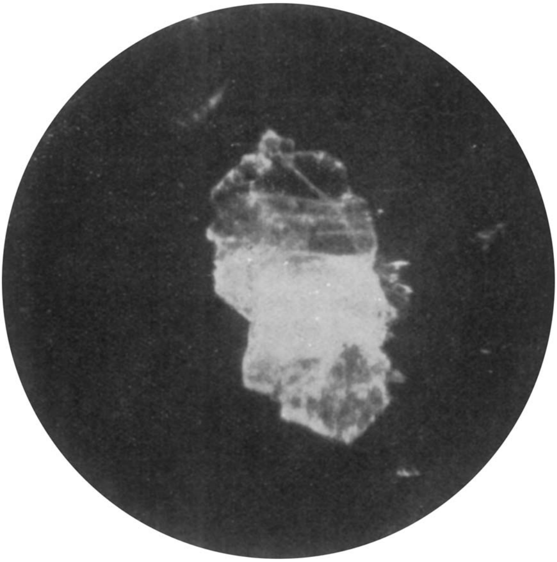

Crystal of potassium hydrogen dioleate. Oblique illumination.
Magnification × 100.