chloride, oxalic acid gradually separated out of the reaction mixture. On distillation trimethyl chloromethane, in one case, and dimethyl ethyl chloromethane in the other, were produced in good yields. On redistillation, the chlorides were readily purified.

Trimethyl chloromethane, $(CH_3)_3CCl$, b. p. 51–52°. Dimethyl ethyl chloromethane, $(CH_3)_2C_2H_5CCl$, b. p. 84–86°.

2. **Triphenyl Carbinol.**—Triphenyl carbinol (2 mols) was dissolved in benzene in an ordinary flask, the stopper of which was fitted with a reflux condenser and a dropping funnel holding the oxalyl chloride (1 mol). On addition of the chloride, instantaneous reaction took place. After warming gently a short time, the mixture was allowed to evaporate and the resulting solid crystallized from benzene. It proved to be triphenyl chloromethane.

Triphenylchloromethane, $(C_6H_5)_3CCl$, m. p. 100–101°.

3. **Pinakone.**—Pinakone (1 mol) was treated directly with oxalyl chloride (1 mol) in an apparatus similar to that used with the primary alcohols. On distillation of the reaction mixture, a liquid boiling between 100–128° resulted, which proved to be impure pinakolin. A reddish residue left in the flask solidified on cooling and crystallized from alcohol in long, white needles, which on analysis were found to be the carbonate of pinakone. M. p. 176–177°.

Calc. for $[(CH_3)_2C]_2CO_3$: C, 58.33%; H, 8.33%. Found: C, 58.34; H, 8.28.

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[CONTRIBUTION FROM THE UNIVERSITY CHEMICAL LABORATORY OF OXFORD.]

THE CRYSTALLIZATION OF CALCIUM TARTRATE.

By F. D. Chattaway.

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Few salts have been more frequently prepared than calcium tartrate on account of its employment for the recognition of the acid and it is therefore surprising to find that little is known of its behavior when crystallizing from aqueous solution. When a soluble calcium salt is added to a neutral solution of a soluble tartrate the compound which first separates is not the ordinary orthorhombic tetrahydrated salt, $C_4H_4O_6Ca.4H_2O$, but a hexahydrated form, $C_4H_4O_6Ca.6H_2O$, which crystallizes in long, slender needles. This is unstable at the ordinary temperature and transforms with loss of two molecules of water into the well known tetrahydrated salt, small crystals of which quickly make their appearance among the needle-shaped crystals and grow at the expense of the latter, which dissolve and ultimately disappear.

Experimental Part.

When equal volumes of 0.2 *N* solutions of calcium chloride and potassium sodium tartrate are mixed the liquid remains clear for a short time,

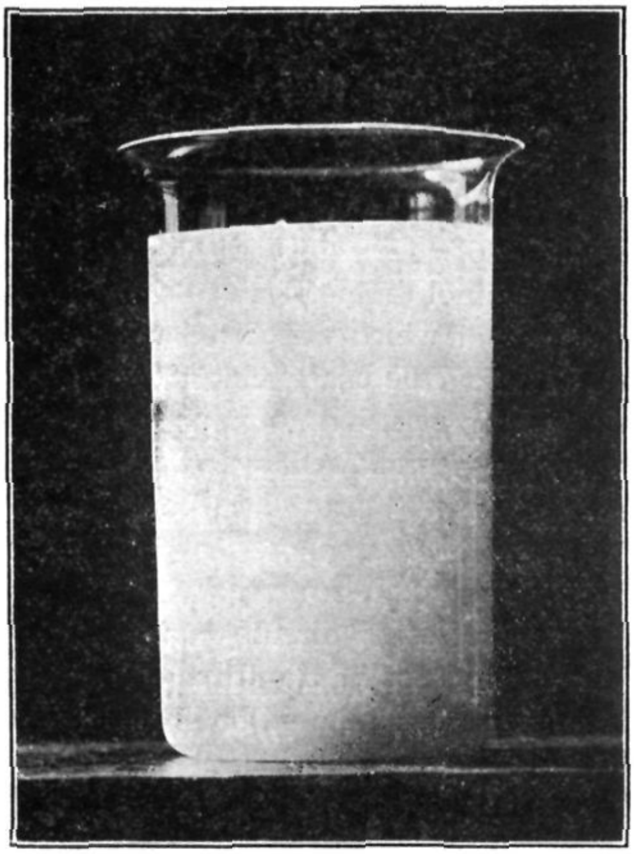

Fig. 1.

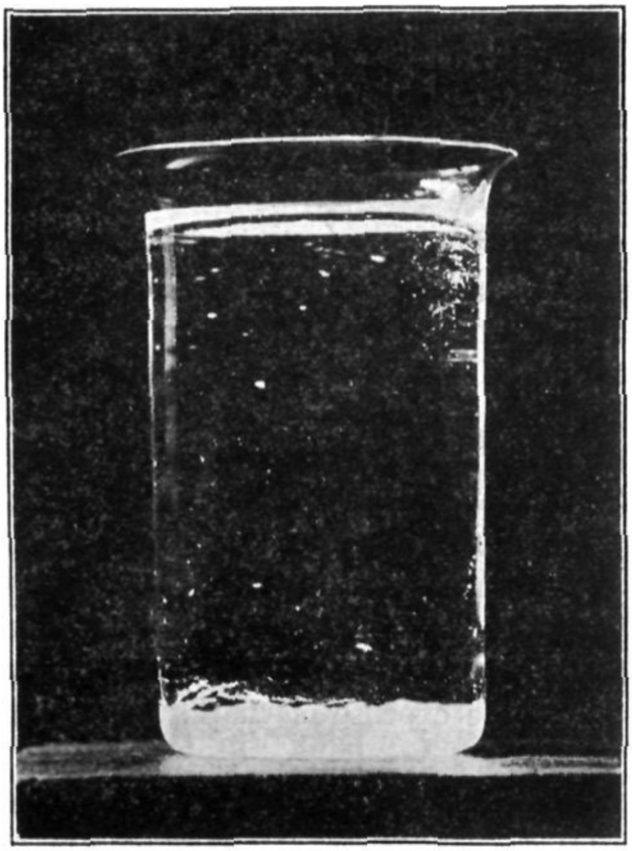

Fig. 2

then small tufts of needle-shaped crystals make their appearance and rapidly grow until in a few minutes the whole is filled with such tufts which finally interlace, a felted mass of crystals resulting which can be inverted without any of the mother liquor escaping. If kept at the ordinary temperature small crystals of the orthorhombic tetrahydrated form of calcium tartrate soon make their appearance and grow rapidly while the unstable needle-shaped crystals dissolve and finally disappear. The orthorhombic crystals thus produced, which are very finely shaped and often of considerable size, sink down in the beaker and form a comparatively thin layer. If the crystalline pulp of needle-shaped crystals be stirred or shaken vigorously, transformation is more rapid and after a few minutes the needle-shaped form is converted into the compact form, the crystals of which having been quickly formed are small and subside on being left at rest as a fine crystalline precipitate.

On gradually warming the felted mass much more rapid transformation takes place, the needle-shaped crystals crumble away, while a shower of small well-shaped rhombic crystals falls to the bottom of the beaker. In the appended plate, Fig. 1 shows a beaker, about half its natural size, filled with a felted mass of needles of the hexahydrated modification immediately after crystallization had taken place. Fig. 2 shows the same beaker 24 hours later after complete transformation of the hexahydrated into the tetrahydrated modification had occurred.

If solutions of lower concentration than 0.2 *N* are mixed, the deposition of the needle-shaped crystals is slower and they are consequently larger in size. Fig. 3 shows a cluster of such crystals about the natural size which separated on mixing one-fifteenth normal solutions and Fig. 4 shows the same cluster after 24 hours when partial transformation had occurred.

When normal solutions of potassium sodium tartrate and calcium chloride are mixed, a slightly flocculent precipitate is at once formed which becomes denser and definitely crystalline as the small needles increase in size. Half normal solutions show the same appearance, the original precipitate being, however, less in amount. When one-third normal solutions are mixed the initial precipitate is very slight while with 0.02 *N* solutions, as above described, the mixed liquid remains clear for a short time until the tufts of needles appear.

The needle-shaped modification which first separates contains 6 molecules of water of crystallization, two of which are

Fig. 3.

Fig. 4.

lost during transformation. For purposes of analysis the hexahydrated crystals prepared as above described by mixing equal amounts of 0.2 *N* solutions of calcium chloride and potassium sodium tartrate were separated by filtration, using a water pump, and thoroughly washed on the filter with distilled water. They were then quickly washed twice with alcohol and once with ether and rapidly pressed between filter paper. The last traces of adhering moisture were removed by exposing them for five minutes over calcium chloride in a vacuum desiccator.

The new form was thus obtained as very fine, colorless needles. When exposed to the air, water was slowly given off, and a crystalline powder of the tetrahydrated form was obtained. When left in a stoppered bottle transformation slowly took place, the crystals became moist, and water was given off which bedewed the sides of the bottle, a crystalline powder of the tetrahydrated form again being produced.

Transformation and loss of water is more rapid at a slightly raised temperature. At the ordinary temperature three or four days' exposure to the air is required before transformation is complete and the weight constant, while at 40° only a few hours' exposure are needed. The crystals of the tetrahydrated form can be heated to 60° in a current of air without any appreciable loss of weight. The loss of water during transformation was estimated by exposing a weighed quantity of the needle-shaped modification to the air until its weight remained constant.

1.5522 lost 0.1884 of water. Loss of water = 12.13%.

The calcium in the needle-shaped modification was estimated by igniting a weighed amount in the air and weighing the calcium oxide obtained.

1.1717 g. gave 0.2227 of calcium oxide. Ca = 13.58%
$C_4H_4O_6Ca.6H_2O$ requires loss of $2H_2O$ = 12.16%. Ca = 13.52%

Mr. T. V. Barker, to whom the thanks of the author are due, has measured some crystals of the orthorhombic tetrahydrated modification obtained by the slow transformation of the hexahydrated form. He found them to be crystallographically identical with those successively examined by Pasteur,[1] by Rammelsberg,[2] and by Hintze.[3]

In confirmation of the work of these observers no hemihedral facets were observed but, as Pasteur notes, absence of geometrical enantiomorphism does not necessarily preclude asymmetry of structure.

The new hexahydrated modification crystallizes in long, very slender, doubly refracting needles with straight extinction and is not suitable for goniometrical examination.

OXFORD, ENGLAND.

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[1] *Ann. chim. phys.*, [3] **24**, 449 (1848).

[2] *Kryst. Phys. Chemie, Abt. II*, 136.

[3] *Ann.*, **226**, 301 (1884).