

zoins. The acidic fraction contained the stilbene- $\alpha,\alpha'$ -bis-thioglycolic acid.

The mixtures of chlorodesoxybenzoins were analyzed as follows. The original chlorodesoxybenzoin mixture (isolated in 55% yield in each case) was recrystallized from ligroin (b. p. 70–90°). The mixture was shown to give the correct carbon and hydrogen analysis. The melting point was determined and also the melting point of the unknown mixture to which had been added a small amount of pure 4- or 4'-chlorodesoxybenzoin. The composition of the mixture was then read from the melting point diagram, the preparation of which is described below. It was shown that crystallization from ligroin did not effect a change in the composition of a known mixture of the two chlorodesoxybenzoins.

The mixture of dimethylaminodesoxybenzoins was separated by a procedure of Jenkins, Bigelow and Buck<sup>11</sup> involving fractional crystallization from ethanolic hydrochloric acid.

**Melting Point Diagram for the System 4-Chlorodesoxybenzoin and 4'-Chlorodesoxybenzoin (Fig. 2).**—A procedure similar to that described by Rheinboldt<sup>12</sup> was used. 4-Chloro- and 4'-chlorobenzoin were prepared by the method of Jenkins<sup>13</sup> and purified by recrystallization from ligroin (b. p. 70–90°). Mixtures totalling 0.500  $\pm$  0.0002 g. were weighed out, brought to complete fusion and cooled slowly while stirring. This fusion was repeated three to five times to ensure adequate mixing. A small portion of each was powdered with an agate mortar and pestle. Samples were introduced into capillary tubes 0.5–1 mm. in diameter and were 4–5 mm. in height. The melting points were determined in an aluminum block which had a lens of high magnifying power so that the samples could be seen clearly. The rate of heating of the block was controlled by a variable voltage transformer. A 360° thermometer, calibrated in degrees, was used. All readings were corrected. The temperature of the block was brought rapidly to within 5° of the melting range, and then allowed to rise at the rate of one degree per ten minutes. The melting point range was recorded as the point where the first liquid appeared (lower curve) and the point where the last crystal disappeared (upper curve). Several samples from the same mixture were taken to determine whether adequate mixing had occurred, and samples were subjected to remelting to prove that no decomposition had occurred during fusion. The m. p. ranges were reproducible to within 1° which corresponded to an error of  $\pm$  4% in composition of the mixture.

**Treatment of Mandelic Acid with Thioglycolic Acid.**—The procedure described for the benzoins was followed except that the reaction mixture was neutralized to congo red paper (acid to litmus) and a sample, withdrawn by pipet and diluted, was titrated with a solution of iodine in ethanol. Titration showed that 92% of the initial thioglycolic acid remained.

**Reaction of Benzoin Methyl Ether with Thioglycolic Acid.**—Benzoin methyl ether was prepared by the method of Fischer.<sup>14</sup> When it was treated in the manner described above for benzoin an 88% yield of desoxybenzoin was obtained, as well as 12% of the stilbene- $\alpha,\beta$ -bis-thioglycolic acid. When a stream of hydrogen chloride was passed into a solution of benzoin methyl ether in acetic acid for thirty minutes at 100° the ether could be recovered quantitatively.

**Ultraviolet Absorption Curves (Fig. 1).**—The instrument used was a Beckman quartz spectrophotometer model DU. The solvent was 95% ethanol and the concentration ranged from 2.5–3.5  $\times$  10<sup>-5</sup> mole per liter. The average deviation in  $\epsilon$  was 0.1, and this corresponded to an error of 1.5% in the region of the maximum.

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(11) Jenkins, Bigelow and Buck, *THIS JOURNAL*, **52**, 4495 (1930).

(12) Rheinboldt, *J. prakt. Chem.*, [2] **111**, 242 (1925).

(13) Jenkins, *THIS JOURNAL*, **66**, 682 (1934).

(14) Fischer, *Ber.*, **26**, 2412 (1893).

## High-Silica Fluosilicic Acids

BY S. MILTON THOMSEN

Current chemical literature teaches that the end-product of the reaction of aqueous hydrofluoric acid on silica, with silica in excess, is fluosilicic acid, having the composition represented by the formula  $H_2SiF_6$ .

Tannanaev,<sup>1</sup> reported in 1936 that more silica may be present in fluosilicic acids (giving them a higher Si/F ratio) than the formula indicates. In agreement with that report, it has been found here that the reaction end-product (silica-saturated fluosilicic acid) has a composition very nearly approaching that represented by the formula  $H_2SiF_6 \cdot SiF_4$  (fluodisilicic acid). Little more than 5 moles of HF suffices to "dissolve" one mole of silica, the product being almost 20% higher in silica than the formula  $H_2SiF_6$  indicates.

Two consequences of the presence of "extra" silica are readily demonstrated: (1) Much heat is evolved when silica-saturated fluosilicic acid is mixed with hydrofluoric acid. The temperature rise is roughly proportional to the amount of extra silica in a less-than-saturated acid. (2) Mixing sodium chloride solution (in excess) with fluosilicic acid produces a granular precipitate of sodium fluosilicate which settles rapidly, followed by a slow precipitation of the extra silica.

Most commercially available fluosilicic acids have compositions approximating that of  $H_2SiF_6$  (30% by weight) and will dissolve approximately 30 g. of silica per liter.

(1) Ivan Tannanaev, *J. Gen. Chem. U. S. S. R.*, **6**, 1430 (1936).

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## Chemical Properties of Berkelium

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The recent production by Thompson, Ghiorso and Seaborg<sup>1</sup> of a radioactive isotope of berkelium (atomic number 97) makes it possible to investigate the chemical properties of this transuranium element by means of the tracer technique. This isotope has been prepared through the bombardment of  $Am^{241}$  with about 35 Mev. helium ions in the 60-inch cyclotron of the Crocker Laboratory and is believed to have the mass number, 243, or possibly 244. This  $Bk^{243}$  has a half-life of 4.6 hours and decays by electron capture with about 0.1% branching decay by alpha-particle emission.

In the present tracer chemical experiments, the radiations accompanying the electron capture process were used as a means of detection and were counted in two ways. Where the sample deposits on the platinum plates were essentially weightless, as was the case following the evapora-

(1) S. G. Thompson, A. Ghiorso and G. T. Seaborg, *Phys. Rev.*, **77**, 838 (1950).