283. *Compounds of Naphthalenesulphinic Acids with their Sodium and Potassium Salts.*

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The isolation of substances containing naphthalenesulphinic acids and their sodium or potassium salts in equimolecular proportion is described, and the evidence that these are compounds of the two components is outlined.

ON addition of dilute hydrochloric acid to the aqueous solution obtained by the reduction of naphthalene-β-sulphonyl chloride with sodium sulphite, a precipitate is immediately formed, which contains naphthalene-β-sulphinic acid and its sodium salt in equimolecular proportion. After recrystallisation of the *substance* from ethyl alcohol, the ratio of these two components is unchanged. Addition of acid to the solution obtained by the similar reduction of naphthalene-α-sulphonyl chloride precipitates naphthalene-α-sulphinic acid. A *substance* containing this acid and its sodium salt in equimolecular proportion is, however, immediately precipitated when dilute hydrochloric acid is added to an aqueous solution of the acid saturated with sodium sulphite. Recrystallisation from alcohol does not affect the ratio of acid to salt, but the product contains alcohol, in place of water, of crystallisation.

On addition of alcoholic potassium hydroxide to an alcoholic solution of naphthalene-β-sulphinic acid, a *substance* which contains the acid and its potassium salt in equimolecular proportion is immediately precipitated, and recrystallisation from ethyl alcohol does not alter the composition. From a cooled alcoholic solution of naphthalene-α-sulphinic acid half-neutralised with potassium hydroxide, a *substance* separates which contains the acid and its potassium salt in equimolecular proportion, together with alcohol of crystallisation; it is unchanged in composition after recrystallisation from ethyl alcohol or chloroform.

The following evidence suggests that these substances are compounds, rather than mixtures, of the acid and the salt: (1) After recrystallisation from solvents in which either the acid or the salt is insoluble, the ratio of these two components is unchanged. (2) The α- and the β-acid melt with decomposition, and immediate blackening, at 96° and 98° respectively. The sodium and potassium complex salts of the α-acid melt at 48° and 38°, respectively, to colourless fluids which at 105° are converted into white solids and become only slightly discoloured at 160°. The corresponding complexes with the β-acid are infusible solids which only become yellow above 160°. When these four substances are contaminated with a trace of free acid, they become blackened at 100°. (3) The sulphinic acids decompose on storage, dinaphthyl disulphoxide being formed after a few weeks, and profound decomposition occurring after several months. The present substances, on the other hand, remain unchanged in m. p. and solubility after 18 months. (4) The smooth thermal decomposition of the compound of naphthalene-α-sulphinic acid and its potassium salt, liberating naphthalene and sulphur dioxide, is not characteristic either of the acid or of the salt.

The occurrence of " acid salts " of monobasic carboxylic acids is well established (see, *e.g.*, Ross, Harrison, and Johnstone, this vol., p. 264; Ekwall, *Kolloid Z.*, 1937, **80**, 77). Their formation also from sulphinic acids is presumably related to the structural similarity between the sulphinyl and the carboxyl group.

Acid potassium salts of monobasic carboxylic acids, like those of the naphthalenesulphinic acids, can be isolated from half-neutralised alcoholic solutions of the acids, and their preparation from benzoic and salicylic acids is described.

EXPERIMENTAL.

Naphthalene-α- and -β-sulphinic acids were prepared by reduction of the sulphonyl chlorides by aqueous sodium sulphite, stored in the form of their iron salts (Thomas, J., 1909, **95**, 344), and converted into the ammonium salts and precipitated with dilute hydrochloric acid when required. The α-acid had m. p. 96°, and after recrystallisation from aqueous alcohol, m. p. 87° (Found, after recrystallisation: S, 15·2. Calc. for $C_{10}H_8O_2S,H_2O$: S, 15·2%). The

m. p. of this acid has been given as 98° by Thomas (*loc. cit.*) and as 85° by Knoevenagel and Kenner (*Ber.*, 1908, **41**, 3319). The β-acid had m. p. 98°; Otto, Rössing, and Troger (*J. pr. Chem.*, 1893, **47**, 95) give 105°, which is the m. p. of di-β-naphthyl disulphoxide (Found: C, 68·1; H, 4·1. Calc. for $C_{20}H_{14}O_2S_2$: C, 68·5; H, 4·0%) obtained by decomposition of the acid on storage, or by thermal decomposition of the acid or its methyl ester. The acid chlorides, prepared from the acids by thionyl chloride, were converted into the methyl esters. Methyl naphthalene-α-sulphinate, described as an oil by Otto and Rössing (*ibid.*, p. 163), crystallised on cooling at 0°; m. p. 44°. The β-ester crystallised spontaneously, m. p. 42° (Otto and Rössing, *loc. cit.*, give m. p. 44°). A mixture of the α- and the β-ester softened at room temperature and liquefied at 32°.

"Acid Salts" of Naphthalene-α-sulphinic Acid.—(i) The *acid sodium* salt (3 g.) was precipitated from a solution of naphthalene-α-sulphinic acid (5 g.) and sodium sulphite crystals (15 g.) in water (50 c.c.) by addition of 5N-hydrochloric acid (25 c.c.). Further addition of acid precipitated the sulphinic acid. The precipitated acid salt had m. p. 75°, effervescing and solidifying at 100° (Found: equiv., 442. $C_{10}H_8O_2S,C_{10}H_7O_2SNa,2H_2O$ requires equiv., 442). After recrystallisation from alcohol, it had m. p. 48°, effervescing and solidifying at 100° (Found: Na, 4·9; loss on heating to constant weight at 95°, 10·3. $C_{10}H_8O_2S,C_{10}H_7O_2SNa,C_2H_6O$ requires Na, 5·1; loss, 10·2%).

(ii) The *acid potassium* salt (5 g.) crystallised from a solution of naphthalene-α-sulphinic acid (5 g.; 1 mol.) in 0·5N-alcoholic potassium hydroxide (26·5 c.c.; 0·5 mol.) on cooling to 0°. After recrystallisation from chloroform, cooled to 0°, it had m. p. 38°, effervescing and solidifying at 105° (Found, for 4 separate preparations: C, 55·3, 55·4, 55·3, 55·4; H, 5·0, 4·8, 4·9, 4·9; S, 12·2; K, 7·6, 7·6; equiv., 528. $C_{10}H_8O_2S,C_{10}H_7O_2SK,2C_2H_6O$ requires C, 56·0; H, 5·2; S, 12·5; K, 7·5%; equiv., 514). The substance was soluble in chloroform, benzene, acetone, toluene, and chlorobenzene, decomposing in the last four solvents with deposition of the normal salt. When heated to constant weight at 93°, it lost 10·2% (Calc. for loss of 1EtOH: 9·8%); the *residue* contained K, 8·5% ($C_{10}H_8O_2S,C_{10}H_7O_2SK,C_2H_6O$ requires K, 8·3%). When heated above 100°, the substance lost weight progressively, with liberation of naphthalene (m. p. and mixed m. p. 80°) and sulphur dioxide.

"Acid Salts" of Naphthalene-β-sulphinic Acid.—(i) *Acid sodium salt.* Addition of excess of hydrochloric acid (5N) to the aqueous solution (500 c.c.) of sodium naphthalene-β-sulphinate, obtained by the reduction of naphthalene-β-sulphonyl chloride (50 g.) with sodium sulphite (100 g.), precipitated the *acid sodium* salt (40 g.). This was soluble in aqueous acetone and in boiling ethyl alcohol, sparingly soluble in cold alcohol. After recrystallisation from 90% ethyl alcohol, it was obtained as colourless needle-shaped crystals, unchanged by heating to 140°, but becoming slightly yellow at 150°, and charring on stronger heating (Found: Na, 5·8; equiv., 412. $C_{10}H_8O_2S,C_{10}H_7O_2SNa$ requires Na, 5·7%; equiv., 406). The substance was decomposed by water, with precipitation of the acid. On addition of a few drops of acetone to the turbid solution, the acid was redissolved and the acid salt crystallised out (Found: Na, 5·4%).

(ii) The *acid potassium* salt (3 g.) crystallised from a solution of naphthalene-β-sulphinic acid (3 g.; 1 mol.) in 0·5N-alcoholic potassium hydroxide (15·9 c.c.; 0·5 mol.) (Found: equiv., 433. $C_{10}H_8O_2S,C_{10}H_7O_2SK$ requires equiv., 422); it crystallised from ethyl alcohol in colourless plates, which were infusible and did not lose weight when heated for 2½ hrs. at 150°. Above that temperature the substance became yellow, and charred on stronger heating (Found: C, 56·2; H, 3·5; K, 9·3; equiv., 422. $C_{10}H_8O_2S,C_{10}H_7O_2SK$ requires C, 56·9; H, 3·5; K, 9·3%). It was soluble in hot water, recrystallising unchanged (Found: K, 9·1%).

Acid Potassium Salt of Benzoic Acid.—On addition of 0·5N-alcoholic potassium hydroxide (16·5 c.c.; 0·5 mol.) to benzoic acid (2 g.; 1 mol.) in ethyl alcohol (25 c.c.) and recrystallisation of the precipitate from ethyl alcohol, the acid *salt* separated as the first crop (1·5 g.) (Found: K, 13·9; equiv., 283. $C_7H_6O_2,C_7H_5O_2K$ requires K, 13·9%; equiv., 282).

Acid Potassium Salt of Salicylic Acid.—This *salt* (2·5 g.) was deposited when an alcoholic solution of salicylic acid (3 g.) half-neutralised with potassium hydroxide (as above) was concentrated at room temperature. After recrystallisation from alcohol, it had m. p. 260° (decomp.) (Found: K, 12·4. $C_7H_6O_3,C_7H_5O_3K$ requires K, 12·4%).

Thanks are due to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries Limited for grants, and to Dr. J. Kenyon, F.R.S., for his interest in this work.

BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, June 22nd,* 1938.]