

**165.** *Chelation in the Potassium Compounds of Carboxylic and Sulphinic Acids.*

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Acid potassium compounds of benzenesulphinic, *p*-toluenesulphinic, and  $\alpha$ - and  $\beta$ -naphthoic acids are described. The first two and the last are ionised salts.  $\alpha$ -Naphthoic acid, however, forms three acid potassium compounds, all showing certain characteristics of chelated substances. These three compounds have the composition 1 : 2, 1 : 1, and 2 : 1 mols. of acid to mols. of normal potassium salt. The last substance shows most signs of chelation, having the lowest melting point and the greatest solubility in solvents of low dielectric constant. A chelated form of potassium *p*-toluenesulphinate is also described.

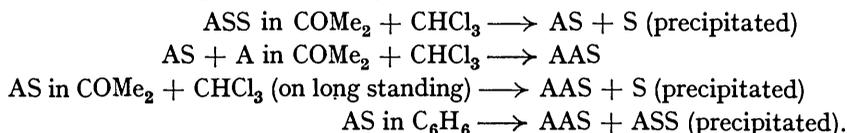
In a previous communication (Balfe and Wright, J., 1938, 1490) acid potassium compounds of  $\alpha$ - and  $\beta$ -naphthalenesulphinic acids were described, and it was evident that the compound of the  $\alpha$ -acid was chelated, whereas that of the  $\beta$ -acid possessed the properties of an ionised salt. Analogous compounds of  $\alpha$ - and  $\beta$ -naphthoic acids have now been prepared and have similar properties, that of the  $\alpha$ -acid showing the characteristics of a chelated compound, being soluble in benzene and chloroform, and melting at a comparatively low temperature, and that of the  $\beta$ -acid showing the characteristics of an ionised salt, charring without melting at a high temperature, and being insoluble in organic solvents of low dielectric constant.

Further experiments are in progress with the object of determining the structure of these compounds.

*Action of Alcoholic Potash on  $\alpha$ - and  $\beta$ -Naphthoic Acids.*—As in the case of  $\beta$ -naphthalenesulphinic acid, addition of 0.5 equiv. of alcoholic potash to a solution of  $\beta$ -naphthoic acid in alcohol produces a copious white precipitate of the acid and its potassium salt in equimolecular proportion which recrystallises unchanged from alcohol in colourless needles.

When 0.5 equiv. of alcoholic potash is added to  $\alpha$ -naphthoic acid, the solution kept for some days without evaporation, and then evaporated in air or on a water-bath, a similar equimolecular compound crystallises (m. p. 163° after recrystallisation from chloroform); but if the mixture is evaporated at once, either in a vacuum or rapidly in air, a mixture of three acid potassium compounds is formed, *viz.*, those in which the ratio acid : normal salt

is (1) 1 : 1, m. p. 163° (referred to as AS); (2) 2 : 1, m. p. 115° (AAS); (3) 1 : 2, m. p. 175° (ASS). These undergo the following reactions :



*Action of Potassium Carbonate on  $\alpha$ -Naphthoic Acid in Benzene Solution.*—The 2 : 1 and the 1 : 2 salt are also produced by adding 0.5 equiv. of potassium carbonate to a dilute solution of  $\alpha$ -naphthoic acid in benzene; a flocculent precipitate of the latter salt slowly separates out, but if the mixture is allowed to stand with occasional stirring, until the potassium carbonate, which can be seen at the bottom, disappears (about 2 hours), the mother-liquor on evaporation yields only the 2 : 1 salt. Long standing, however, leads to formation of the normal salt in the precipitate,  $\alpha$ -naphthoic acid being found in the solution. This change is probably due to dissociation of the 1 : 2 salt, for the 2 : 1 salt is unchanged by repeated crystallisation from benzene, in which the normal salt is insoluble.

That the three acidic potassium compounds of  $\alpha$ -naphthoic acid are not mixtures of the acid and its potassium salt, or of either of these with one or two acid salts is shown by the following facts: (1) All have sharp m. p.'s and although several different methods of preparation have been used for each substance, the m. p.'s and potassium contents have been constant. (2) AS and AAS are both soluble in benzene and chloroform, whereas the normal salt is insoluble in both these solvents. (3) ASS is not a mixture of S with either A or AS, because it is only slightly soluble in chloroform and not at all in benzene, whereas AS and the acid are very soluble in both solvents. (4) On recrystallisation from solvents in which one of the components is very soluble, successive fractions have the same m. p. All three potassium compounds of  $\alpha$ -naphthoic acid decompose in the same manner on heating, melting and giving off acid vapours and then turning brown, effervescing, and giving off naphthalene. Since potassium  $\alpha$ -naphthoate, on heating, melts, turns brown, effervesces, and gives off naphthalene, it is probable that the acid compounds break up into the acid and potassium salt at high temperatures, the acid subliming out and the salt decomposing to form naphthalene. This differs from the behaviour of the acid potassium compounds of  $\alpha$ - and  $\beta$ -naphthalenesulphinic acid, which do not regenerate the acid when heated. Acid potassium  $\alpha$ -naphthalenesulphinate, however, effervesces and gives off naphthalene at a comparatively low temperature (J., 1938, 1490).

*Acid Potassium Compounds of Benzenesulphinic and *p*-Toluenesulphinic Acids.*—These compounds are formed in solution when the acids are half-neutralised with alcoholic potash. The compound of benzenesulphinic acid with its potassium salt is obtained on evaporating the solution to dryness, and crystallises unchanged from alcohol; and the corresponding *p*-toluenesulphinic compound crystallises in long needles on cooling the generating solution below 0°.

These compounds are extremely stable, and are unchanged by long heating at 150°. Above this temperature they show the characteristic charring of an ionised salt, without melting. The acid potassium compound of *p*-toluenesulphinic acid, however, is very soluble in chloroform, the solution decomposing on standing.

*Chelation in Normal Potassium *p*-Toluenesulphinate.*—Potassium *p*-toluenesulphinate melts on strong heating, unlike the acid salt, which chars. Moreover, it is soluble in chloroform, crystallising from this solvent in long needles; if excess is present in the boiling solution, the undissolved salt melts under the solution to a colourless globule, which is found to be unchanged in composition on cooling, but the crystals so obtained cannot be melted again at the same temperature by heating in air, so a chelated variety is evidently formed, which can only exist under the chloroform solution. This phenomenon may account for the solubility of the acid potassium compound in chloroform, a property which is not characteristic of those acidic potassium compounds which char on heating.

Potassium *p*-toluenesulphinate which has been melted under chloroform solidifies in the anhydrous form, whereas the needles which separate from the chloroform solution on cooling are of the *monohydrate*.

## EXPERIMENTAL.

$\alpha$ - and  $\beta$ -Naphthoic acids were purified by recrystallisation from alcohol. Benzenesulphinic acid was prepared by the Friedel-Crafts reaction from benzene previously dried with sodium. *p*-Toluenesulphinic acid was precipitated from the sodium salt.

Potassium *p*-toluenesulphinate was described as a dihydrate by Otto and Rössing (*Ber.*, 1887, 20, 2088) but the crystals obtained from solution in chloroform are the *monohydrate* (Found: K, 18.53; loss at 100°, 8.6.  $C_7H_7O_2SK \cdot H_2O$  requires K, 18.4;  $H_2O$ , 8.5%).

The acid potassium salt of  $\beta$ -naphthoic acid (3.5 g.) was precipitated when  $\beta$ -naphthoic acid (3.2569 g.), dissolved in alcohol, was half-neutralised with 35.61 c.c. of alcoholic potash, standardised by titration against  $\beta$ -naphthoic acid (0.2410 g. of acid = 5.27 c.c.). The precipitate was redissolved by boiling with more alcohol, and crystallised on cooling in fine needles (Found: K, 10.05.  $C_{11}H_8O_2 \cdot C_{11}H_7O_2K$  requires K, 10.2%). The substance was unchanged by heating at 150°, and charred without melting at a high temperature.

*Potassium Salts of  $\alpha$ -Naphthoic Acid.*—(1) *Potassium  $\alpha$ -naphthoate* (1.2 g.) crystallised from a mixture of ASS (1.224 g.) and AAS (1.148 g.) after boiling in alcohol-benzene, in microscopic rectangular prisms (m. p. 240°). It was precipitated in plates when ASS was dissolved in acetone and chloroform added (Found: K, 18.3.  $C_{11}H_7O_2K$  requires K, 18.6%). It was very soluble in water, alcohol, and acetone, and insoluble in benzene and chloroform. It decomposed at a high temperature with effervescence and evolution of naphthalene.

(2) *Acid potassium  $\alpha$ -naphthoate* (AS). (i)  $\alpha$ -Naphthoic acid (1.199 g.) was half-neutralised with alcoholic potash (7.73 c.c.) which had been standardised by titration with  $\alpha$ -naphthoic acid (0.1977 g. = 2.55 c.c.); the mixture was kept for 2 days without evaporation, and then allowed to evaporate in air, colourless prisms (1 g.) being formed, m. p. 163° after recrystallisation from chloroform (Found: K, 10.1.  $C_{11}H_8O_2 \cdot C_{11}H_7O_2K$  requires K, 10.2%).

(ii)  $\alpha$ -Naphthoic acid (1.3521 g.) was half-neutralised with 8.719 c.c. of the same alcoholic potash, the mixture evaporated to dryness in a vacuum, the residue washed with chloroform to remove other acid potassium compounds, the remaining ASS dissolved in acetone, and chloroform added; the precipitated potassium  $\alpha$ -naphthoate was filtered off, and the mother-liquor evaporated, two fractions of AS being obtained (0.5 g.), both melting at 163° (Found: K, 10.1; equiv., 384.  $C_{11}H_8O_2 \cdot C_{11}H_7O_2K$  requires K, 10.2%; equiv., 382). The acid salt was soluble in alcohol, acetone, chloroform, and benzene, decomposing in the last to form AAS and ASS. It was slowly decomposed when shaken with water, to form  $\alpha$ -naphthoic acid and the normal potassium salt.

(3) *Diacid potassium  $\alpha$ -naphthoate* (AAS) (0.2 g.) separated as a soapy white solid when  $\alpha$ -naphthoic acid (0.588 g.), dissolved in benzene, was half-neutralised by addition of 3.68 c.c. of alcoholic potash (7 c.c.  $\equiv$  0.5589 g. of acid), and the mixture allowed to evaporate slowly. The substance crystallised from benzene in colourless prisms, m. p. 115° (Found: K, 6.9.  $2C_{11}H_8O_2 \cdot C_{11}H_7O_2K$  requires K, 7.0%). It was also produced when  $\alpha$ -naphthoic acid (3.2393 g.) was half-neutralised by addition of 35.95 c.c. of alcoholic potash (0.2478 g. of acid  $\equiv$  5.5 c.c.) and the solid obtained was dissolved in acetone, and chloroform added. The precipitated potassium  $\alpha$ -naphthoate was filtered off, and the mother-liquor evaporated to dryness. After recrystallisation from benzene, the crystals had m. p. 115° (Found: K, 7.05%). The same salt (0.4 g.) was also produced when  $\alpha$ -naphthoic acid (0.5260 g.) was dissolved in alcohol and  $\frac{1}{2}$  equiv. of alcoholic potash added; the mixture was evaporated to dryness, the residue dissolved in acetone, and chloroform added. There was no precipitate of potassium  $\alpha$ -naphthoate, and on concentrating the solution, AAS separated out, m. p. 115° (Found: equiv., 277.  $2C_{11}H_8O_2 \cdot C_{11}H_7O_2K$  requires equiv., 277). When to  $\alpha$ -naphthoic acid (2.0100 g.), dissolved in hot benzene (100 c.c., previously dried with sodium),  $\frac{3}{8}$  equiv. of dry potassium carbonate (0.5383 g.) was added, and the mixture boiled and set aside for 4 hours, the mother-liquor after removal of precipitated potassium  $\alpha$ -naphthoate afforded the AAS salt; after recrystallisation from benzene, it had m. p. 115°.

The diacid potassium  $\alpha$ -naphthoate was very soluble in and stable in alcohol, acetone, benzene, and chloroform. It was decomposed on boiling with water into  $\alpha$ -naphthoic acid and potassium  $\alpha$ -naphthoate. It decomposed at a high temperature giving off acid fumes, and then effervescing and giving off naphthalene.

(4) *Acid dipotassium  $\alpha$ -naphthoate* (ASS) was formed when  $\alpha$ -naphthoic acid (0.9181 g.) was half-neutralised with 5.92 c.c. of alcoholic potash (2.55 c.c.  $\equiv$  0.1977 g. of acid). The mixture was evaporated to dryness in a vacuum, and the resulting solid extracted with chloroform. The pure salt separated from the extract on standing in a warm place; m. p. 175° (Found: K, 13.2.  $C_{11}H_8O_2 \cdot 2C_{11}H_7O_2K$  requires K, 13.2%). The solid remaining after the chloroform

washing was dissolved in cold alcohol and benzene, and on evaporation a very fine precipitate separated, m. p. 175° (Found : equiv., 598.  $C_{11}H_8O_2, 2C_{11}H_7O_2K$  requires equiv., 592).

The same salt was also formed when  $\alpha$ -naphthoic acid (2.086 g.) was dissolved in benzene (200 c.c., previously dried with sodium) and 0.5 equiv. of dry potassium carbonate (0.4198 g.) added. The mixture was kept for 2 hours with occasional stirring, and the flocculent precipitate of ASS was filtered off, dissolved in alcohol, and the solution filtered from traces of potassium carbonate; the solution was evaporated to dryness, and the residue dissolved in acetone; on addition of benzene, ASS slowly separated out; m. p. 175°. It was also produced (m. p. 175°), together with AAS, when AS was kept for 3 hours in benzene solution, or was boiled in benzene.

Acid dipotassium  $\alpha$ -naphthoate is an amorphous white solid, soluble in alcohol and acetone and slowly decomposed by water into  $\alpha$ -naphthoic acid and potassium  $\alpha$ -naphthoate. It is insoluble in benzene, very slightly soluble in chloroform, and is decomposed into S and AS in acetone-chloroform. On heating it melts, giving off acid fumes, and finally effervesces and gives off naphthalene.

*Acid Potassium Salt of Benzenesulphinic Acid.*—This salt was produced when benzenesulphinic acid (2.440 g.) was dissolved in alcohol (10 c.c.) and half-neutralised with 11.71 c.c. of alcoholic potash (0.04109 g. KOH per c.c.), the mixture being evaporated to dryness and the residue recrystallised from alcohol (Found : K, 12.3.  $C_6H_6O_2S, C_6H_5O_2SK$  requires K, 12.1%). It is a crystalline solid, soluble in alcohol and insoluble in water and benzene. It chars without melting when heated.

*Acid Potassium Salt of p-Toluenesulphinic Acid.*—When *p*-toluenesulphinic acid (5.887 g.) was half-neutralised by addition of 40.78 c.c. of alcoholic potash (24.9 c.c.  $\equiv$  1.7972 g. of acid) and the solution cooled to 0°, large needles crystallised out (Found : K, 11.0.  $C_7H_8O_2S, C_7H_7O_2SK$  requires K, 11.1%). This salt was very soluble in alcohol and in chloroform, decomposing in the latter. It was slowly decomposed by hot water into its constituent acid and normal salt. When heated, the crystals lost their brightness and very slowly charred.

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