

**147. Molecular Weight and Structure of the Acid Potassium Compounds of  $\alpha$ - and  $\beta$ -Naphthalenesulphinic Acids.**

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The compound of  $\alpha$ -naphthalenesulphinic acid with its potassium salt is shown to be the acid salt of the hexamer. Decomposition products of this compound in solution are described containing varying proportions of the acid and the potassium salt. The bond O-K $\leftarrow$ O is found to be very stable, and to confer on the compounds certain properties resembling those of the acid potassium compound of  $\beta$ -naphthalenesulphinic acid. A structure is suggested for this compound.

$\alpha$ -NAPHTHALENESULPHINIC acid forms a compound with its potassium salt which crystallises with two molecules of alcohol one being retained on heating up to 105°. The substance melts at 38°, is soluble in organic solvents and insoluble in water. The analogous compound of the  $\beta$ -acid contains no alcohol, is insoluble in cold water, and neither melts nor dissolves in organic solvents (Balfe and Wright, *J.*, 1938, 1490; Wright, *J.*, 1942, 263).

In order to find the reason for this great difference, the behaviour and molecular weight of the  $\alpha$ -compound in organic solvents have been investigated.

In nitrobenzene the complex is shown to be  $\alpha$ -(AK,alc.)<sub>6</sub> where "A" represents a molecule of the acid, and "K" represents a molecule of the potassium salt. Unless otherwise stated, all experiments have been carried out with the substance  $\alpha$ -(AK,alc.)<sub>6</sub> and not with the substance  $\alpha$ -(AK,2alc.)<sub>6</sub>, as the second molecule of alcohol is lost at the melting point, or on desiccation, and cannot, therefore, be regarded as part of the structure of the complex.

Decomposition in dilute benzene solutions is too rapid to allow of molecular-weight determinations in this solvent, but an examination of the decomposition products throws much light on the structure of both the  $\alpha$ - and the  $\beta$ -acid compound.

The  $\alpha$ -compound undergoes progressive decomposition in benzene solution, the rate of degradation and the nature of the products varying with the concentration, the temperature, and the dryness of the solution. No uniform behaviour has been observed, but, in general,  $\alpha$ -AKKK separates from the more concentrated solutions,  $\alpha$ -AKK from the more dilute solutions, and  $\alpha$ -AAKKK from mother liquors after separation and filtration of the other compounds.

These three *substances* may be characterised as compounds and not mixtures of the acid and potassium salt, or of one another, by their behaviour on heating, and by their solubilities in water.

1. None shows the charring at a little over 100° characteristic of the acids.

2.  $\alpha$ -AKKK has been obtained in two successive fractions from the same mother liquor; it is soluble in water, but decomposed on dilution. It yields no naphthalene on heating, until 200° is reached, and is only slightly darkened at this temperature. It cannot, therefore, be a mixture of A and K, AK and K, or AKK and K, as both AK and AKK give naphthalene on being heated to 105° and 100° respectively.

3.  $\alpha$ -AKK is decomposed by water, yields naphthalene at 100°, but does not melt or char until *ca.* 185° is reached. It cannot, therefore, be a mixture of K and A, or K and AK.

4.  $\alpha$ -AAKKK is soluble in water, without decomposition, is uncharred until 170° is reached, and yields no naphthalene on being heated, so it cannot be a mixture of A and K, AK and AKK, or A and AKKK.

The presence of other complexes in the solutions, containing a larger proportion of acid, is inferred from a comparison of the very low solubility of the acid in benzene (less than 0.0108

mole per 1000 g. of solvent, see previous paper) with the weight of acid retained in the solution from which these potassium complexes have separated (0.217 mole per 1000 g. of solution, p. 695). Moreover, this retention of sparingly soluble acid, and insoluble potassium salt in solution, precludes the possibility that  $\alpha$ -(AK,alc.)<sub>6</sub> breaks down into molecules of the normal potassium salt and the acid, and that these molecules undergo rearrangement to form the complexes isolated. As these substances contain no alcohol, it is assumed that loss of alcohol precedes the disintegration of the complex.  $\alpha$ -AKK does, in fact, separate with two molecules of water from an undried benzene solution of  $\alpha$ -(AK,alc.)<sub>6</sub>. The alcohol is also progressively lost by desiccation or under reduced pressure. At 20 mm./40—42° a constant weight is reached at the end of about 3 hours, and the composition of the resultant substance is found to be  $\delta$ (AK)<sub>3</sub>alc. At 30°/ < 2 mm. the same substance is produced, whilst at 40°/ < 2 mm. the alcohol content is lowered to two molecules. On leaving (AK,alc.)<sub>6</sub> in a vacuum desiccator for ten days,  $\delta$ (AK)<sub>3</sub>alc. is again produced, and at the end of three weeks all the alcohol is lost, and a thick gum is formed, which is still soluble in benzene, and gives the original substance on treatment with alcohol. The substance  $\alpha$ -(AK)<sub>6</sub> is less stable in organic solvents than  $\alpha$ -(AK,alc.)<sub>6</sub>, but gives similar complexes on decomposition.

A substance having the composition  $\alpha$ -AKK, 3H<sub>2</sub>O has been synthesised by the addition of  $\frac{3}{2}$  of an equivalent of alcoholic potash to  $\alpha$ -naphthalenesulphinic acid. This substance separates from the aqueous alcoholic solution. It melts at 45°, is soluble in organic solvents, and possesses all the properties of a chelated compound. When it is warmed to 48°, one molecule of water is lost, and the substance immediately solidifies, becomes insoluble in organic solvents, and regains all the characteristics of the anhydrous compound, and of the dihydrate, obtained by the decomposition of  $\alpha$ -(AK,alc.)<sub>6</sub> in benzene solution. On desiccation at room temperature the trihydrate begins to melt, as it becomes mixed with its decomposition product  $\alpha$ -AKK, 2H<sub>2</sub>O. This substance is obtained fully crystalline after two days' desiccation at room temperature over calcium chloride.

It is evident that, in these decomposition products of  $\alpha$ -(AK,alc.)<sub>6</sub>, the potassium atom is present in three states :

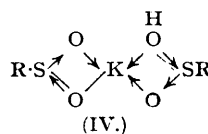
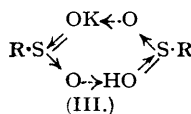
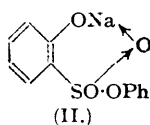
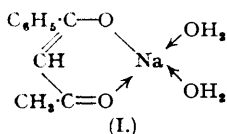
1. As an ion, in those compounds soluble in water, *e.g.*, at least one of the atoms of potassium in  $\alpha$ -AKKK and  $\alpha$ -AAKKK.

2. As a link connecting molecules of the potassium salt with one another, and/or with the acid, the resulting compound having a low melting point, and being soluble in organic solvents and insoluble in water, *e.g.*, in  $\alpha$ -(AK,alc.)<sub>6</sub>,  $\alpha$ -(AK)<sub>6</sub>, and  $\alpha$ -AKK, 3H<sub>2</sub>O. These potassium atoms are probably surrounded by a complete octet of electrons in the manner made familiar by many sodium compounds having similar properties, *e.g.*, the sodium compound of benzoyl acetone (I) (Sidgwick and Brewer, *J.*, 1925, 127, 2379). The potassium atoms probably complete their octets by some space arrangement of molecules whereby the necessary electrons are attracted from the oxygen atoms of the carboxylic group and the alcohol. As many such arrangements are possible, no one is indicated.

That the molecules of potassium salt may be connected with one another, and not only through the acid, is indicated by the formation of such a compound as  $\alpha$ -AKKK from  $\alpha$ -(AK,alc.)<sub>6</sub> and by the fact that the normal potassium salt of toluene-*p*-sulphinic acid melts to a clear liquid under chloroform, but returns to the familiar unmelting salt on removal of the chloroform (Wright, *J.*, 1940, 860). Some complex is obviously formed involving co-ordination through the potassium atom.

3. As a link connecting molecules of potassium salt with one another and/or with the acid, producing compounds which are insoluble or sparingly soluble in both water and most organic compounds, soluble in chloroform, and much more sparingly soluble in alcohol than the normal potassium salt. They are very stable, and unchanged by prolonged heating at 150—200°, *e.g.*, in  $\alpha$ -AKK,  $\alpha$ -AKK, 2H<sub>2</sub>O, and the potassium atoms connecting the molecules in  $\alpha$ -AKKK and  $\alpha$ -AAKKK.

That  $\alpha$ -AKK, 3H<sub>2</sub>O changes from type "2" to type "3" on the loss of one molecule of water at such a low temperature as 48° indicates that the difference is one of the number of electrons round the potassium atom only, and O—K←O is suggested for this stable link.



Additional evidence is offered by a comparison with the sodium derivative of the phenyl ester of phenyl *o*-hydroxyphenylsulphonate, which has the structure (II), and possesses similar properties, *viz.*, m. p. 220—230°, ready solubility in chloroform, sparing solubility in organic solvents; and with a similar derivative of phenyl salicylate, which has m. p. 193—195° and is sparingly soluble in water (Tozer and Smiles, *J.*, 1938, 1897).

From its similarity to all these compounds in group "3," (III) is suggested for the structure of  $\beta$ -AK. Evidence of the hydrogen bond in both  $\alpha$ -(AK,alc.)<sub>6</sub> and  $\beta$ -AK is found in the fact, that although both acids form stable brucine salts in cold alcoholic solution, the acid potassium compounds are not affected by brucine in alcohol at ordinary temperatures.

On heating  $\alpha$ -(AK,alc.)<sub>6</sub> to 105°, some sulphur dioxide and naphthalene are liberated, and quantitative determinations have revealed that only one molecule of acid decomposes in this way, the rest of the complex disintegrating, at the same time, into a mixture of potassium hydrogen sulphate,  $\alpha\alpha'$ -naphthyl disulphoxide, and a yellow substance not identified.

*Conclusion.*—The difference between the acid potassium compound of the  $\alpha$ -acid and that of the  $\beta$ -acid is found in the fact that, since the  $\alpha$ -compound is a complex composed of many molecules, with many ways in which electrons can be attracted from neighbouring oxygen atoms, the potassium atom in it is completely chelated, and the compound has the properties associated with such an arrangement.

The  $\beta$ -compound, from its similarity to compounds known to possess a single group O—Na←O, and to compounds produced by the degradation of the  $\alpha$ -compound having similar properties, has a structure in which the potassium atom is co-ordinated with one oxygen atom only, as O—K←O.

It is suggested that the inability of the single acid potassium molecule to form a compound containing a completely chelated potassium atom, is evidence that the four-membered ring (IV) cannot be formed.

#### EXPERIMENTAL.

The method of molecular-weight determination has been described (previous paper). Nitrobenzene containing moisture was used, as  $\alpha$ -(AK,alc.)<sub>6</sub> is more stable in the damp than in the dry solvent. The solution remained clear for the duration of the experiment, but after some hours became cloudy, with deposition of the normal potassium salt. This was accompanied by a large depression in the freezing point, owing to release of alcohol in the solution.

The  $\alpha$ -(AK,alc.)<sub>6</sub> was prepared by the addition of  $\frac{1}{2}$  equivalent of alcoholic potash to the acid crystals, and evaporation of the resultant solution in a vacuum desiccator in a refrigerator. The substance is only produced by slow evaporation at low temperatures.

Wherever a deposition of normal potassium salt is recorded, the composition of the substance was ascertained by a potassium determination. The acid was identified by the determination of a mixed melting point with a pure specimen.

For the molecular weight of the acid potassium compound of  $\alpha$ -naphthalenesulphinic acid in nitrobenzene, the following results were obtained: (a) moles per 1000, 0.0172;  $\Delta T$ , 0.020°;  $M/M_0$  (see previous paper), 6.06; (b) moles per 1000, 0.0306;  $\Delta T$ , 0.036;  $M/M_0$ , 5.99.

*Acid Potassium Compounds of  $\alpha$ -Naphthalenesulphinic Acid.*—Compound  $\alpha$ -AKK. (AK,alc.)<sub>6</sub> (0.5 g.) was dissolved in dry benzene (17.5 g.). Rapid decomposition took place, with deposition of the compound  $\alpha$ -AKK (Found: K, 12.18.  $C_{30}H_{28}O_8S_3K_2$  requires K, 11.96%).

(AK,alc.)<sub>6</sub> (0.35 g.) was dissolved in dry benzene (17 g.);  $\alpha$ -AKK was deposited. After being washed with ether, this gave K, 12.23%. This compound was insoluble in organic solvents, and was unmelted at 180°. It was insoluble in water, and slowly decomposed in water with precipitation of the acid. It was sparingly soluble in alcohol.

*Compound  $\alpha$ -AKK, 3H<sub>2</sub>O.* The trihydrate was formed when alcoholic potash (16.4 c.c., 0.357N,  $\frac{2}{3}$  mol.) was added to the acid (1.686 g., 1 mol.), and the solution evaporated to dryness and washed with ether. The substance, m. p. 45° [Found: C, 50.8; H, 3.78; K, 11.26; loss at 48°, 2.26.  $C_{30}H_{28}O_8S_3K_2 \cdot 3H_2O$  requires C, 51.0; H, 3.97; K, 11.05; loss of H<sub>2</sub>O, 2.55], was soluble in benzene and chloroform, decomposing in hot chloroform, with deposition of the normal potassium salt. In a vacuum, or at 48°, it first melted and then solidified, forming the dihydrate. At 100° some naphthalene was slowly evolved. The compound was decomposed by water, with precipitation of the acid.

*Compound  $\alpha$ -AKK, 2H<sub>2</sub>O.* The dihydrate was produced when the trihydrate was kept in a vacuum, in a refrigerator, for 48 hours. It was decomposed by water with precipitation of the acid, and was insoluble in benzene, and soluble in chloroform. It was unmelted and uncharred at 170°, at which temperature it turned yellow. It charred at 185°. On prolonged heating at 100° some naphthalene was evolved (Found: K, 11.54.  $C_{30}H_{26}O_8S_3K_2 \cdot 2H_2O$  requires K, 11.34%).

The compound was also formed when a solution of (AK,alc.)<sub>6</sub> in chloroform was allowed to stand, filtered from the precipitated potassium salt, and evaporated to dryness, and the residue washed with ether to remove acid (Found: K, 11.38%); when a solution of  $\alpha$ -(AK,alc.)<sub>6</sub> in benzene was evaporated to dryness, and the residue washed with ether (Found: K, 11.5%); and when  $\alpha$ -(AK,alc.)<sub>6</sub> was rubbed with a little benzene and then washed with benzene (Found: K, 11.25%).

Dry solvents were not used, and water was apparently taken from these, or from the air, or both.

*Compound  $\alpha$ -AKKK.* This (0.9088 g.) was precipitated when  $\alpha$ -(AK,alc.)<sub>6</sub> (2.18 g.) was dissolved in benzene (12.77 g.) and kept at 6.0° until the freezing point of the mixture was constant, *i.e.*, until no further precipitate was being formed. The precipitate was filtered off and washed with benzene. It

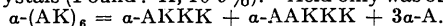
was soluble in absolute alcohol, but decomposed on standing with deposition of the normal potassium salt. It was soluble in a little water, but decomposed on dilution with precipitation of the acid.

The compound was insoluble in organic solvents, and did not lose naphthalene at 100°. It was unchanged by prolonged heating at 180° but was slightly darkened at 200° (Found: K, 13.47.  $C_{40}H_{39}O_8S_4K_3$  requires K, 13.27%). The calculated weight of acid remaining in solution after the precipitation of this substance was 0.217 mole per 1000 (cf. the solubility of the free acid, less than 0.0108 mole per 1000; previous paper).

On evaporating this mother liquor a further crop of crystals was obtained having the same composition after being washed with ether (Found: K, 13.42%). Acid only was found in the residue. This substance was also precipitated when  $(AK,alc.)_6$ , which was kept in a vacuum desiccator until all alcohol was lost, was dissolved in benzene (Found: K, 13.5%).

**Compound  $\alpha$ -AAKKK.** This was precipitated when  $\alpha$ - $(AK,alc.)_6$  (0.1406 g.) was dissolved in benzene (12.77 g.) and kept at 6°. It was soluble and stable in water, the solution being acid to litmus. It was insoluble in organic solvents, and uncharred at 180°. It did not lose naphthalene at 100° (Found: K, 10.11.  $C_{50}H_{37}O_{10}S_2K_3$  requires K, 10.9%).

It was also produced when  $\alpha$ - $(AK,alc.)_6$ , which had lost all alcohol in a vacuum at 40° was dissolved in benzene, and the precipitated  $\alpha$ -AKKK filtered off. The solution was stable for some hours;  $\alpha$ -AAKKK then separated in beautiful crystals (Found: K, 10.9%). Acid only was obtained from the mother liquor.



**Brucine  $\alpha$ -Naphthalenesulphinic Dialcoholate.**—This compound was formed when brucine (2.95 g., 1 mol.) and  $\alpha$ -naphthalenesulphinic acid (1.44 g., 1 mol.) were mixed in cold alcohol. A white solid slowly separated, m. p. 168° (Found, after recrystallisation from absolute alcohol: S, 4.27.  $C_{37}H_{45}O_8N_2S$  requires S, 4.7%).

**Stability of  $\alpha$ - $(AK,alc.)_6$  in Brucine Solution.**— $\alpha$ - $(AK,alc.)_6$  (8.16 g., 1 mol.) and brucine (8.125 g., 1 mol.) were dissolved in alcohol and left in a desiccator for 1 week. A mixture of crystals and gum was produced. The crystals were found to be unchanged brucine (after recrystallisation from alcohol, and drying, m. p. and mixed m. p. with original brucine, 175°). The gum was soluble in chloroform, and  $\alpha$ - $(AK,alc.)_6$  was obtained from this solution, m. p. 38°; *i.e.*, there was no reaction between the two substances in the cold. On boiling a mixture of the two substances in alcohol, evaporating the solution, and extracting the residue with alcohol, very sparingly soluble crystals of the brucine sulphinate were deposited (m. p. 168°) and normal potassium  $\alpha$ -naphthalenesulphinic acid was recovered from the mother liquor.

**Brucine  $\beta$ -Naphthalenesulphinic Acid.**— $\beta$ -Naphthalenesulphinic acid (1.177 g., 1 mol.) and dried brucine (2.415 g., 1 mol.) were dissolved in alcohol and evaporated to dryness in a desiccator. The residue was dissolved in a small volume of alcohol, in which it was very soluble, added to an equal volume of water, and allowed to evaporate slowly in a desiccator. Very large crystals of the dihydrate of brucine  $\beta$ -naphthalenesulphinic acid were formed, which, on further desiccation dropped to pieces, with the formation of the monohydrate.

For the dihydrate (Found: loss at 100°, 5.39.  $C_{33}H_{34}O_6N_2S, H_2O$  requires loss of  $2H_2O$ , 5.79%). For the monohydrate (Found: S, 5.02; loss at 100°, 3.13.  $C_{33}H_{34}O_6N_2S, H_2O$  requires S, 5.20; loss of  $H_2O$ , 2.98%). For the anhydrous compound (Found: M (by titration), 583.  $C_{33}H_{34}O_6N_2S$  requires M, 586).

**Stability of  $\beta$ -AK in Brucine Solution.**—Brucine (1.6 g., 1 mol.) was dissolved in alcohol, and  $\beta$ -AK (1.45 g., 1 mol.) was added.  $\beta$ -AK is very sparingly soluble in alcohol, whereas the brucine salt of the acid is very soluble. After 2 days, the  $\beta$ -AK was still undissolved, showing that it was unacted upon by the brucine at ordinary temperatures. The mixture was then refluxed for  $\frac{1}{2}$  hour; solution was then complete. On evaporation, cubical crystals were deposited first. After long drying in a vacuum these gave M (by titration), 574; *i.e.*, the normal brucine salt had been formed. From the very small mother liquor, needle-shaped crystals of the normal potassium salt separated.

**Decomposition of  $\alpha$ - $(AK,alc.)_6$ , 6alc.**—Crystals of this substance were heated in a U-tube in a current of nitrogen which had previously been bubbled through a guard tube containing barium chloride. After passing through the U-tube the nitrogen was bubbled through two bottles containing hydrogen peroxide, and finally through a guard tube containing barium chloride. There was no precipitate formed in the latter. The U-tube was heated for  $2\frac{1}{2}$  hours at 140° in an oil-bath; naphthalene then collected in the leading tubes (m. p. and mixed m. p. 80°). The hydrogen peroxide solutions were then titrated against standard sodium hydroxide solution (Found: loss in weight, 24.4;  $SO_2$ , 2.25. Calc. for loss of 12 alc., 1 mol. of  $C_{10}H_8$ , 1 mol. of  $SO_2$ : loss, 24.1;  $SO_2$ , 2.08%).

**Removal of Alcohol from  $\alpha$ - $(AK,alc.)_6$  and  $\alpha$ - $(AK,alc.)_6$ , 6alc.**— $\alpha$ - $(AK,alc.)_6$ , 6alc. was heated to 40–42° in a tube, connected with a water pump, for 6 hours (Found: loss, 13.6. Calc. for loss of 9 alc.: loss, 13.35%).  $\alpha$ - $(AK,alc.)_6$  was (i) heated to 30° in a tube connected with a high vacuum pump, until the weight was constant (Found: loss, 4.78%); (ii) left in a vacuum desiccator for 10 days (Found: loss, 4.35. Calc. for loss of 3 alc.: loss, 4.91%).

**Production of  $\alpha$ - $(AK)_2$ , 2alc.**— $\alpha$ - $(AK,alc.)_6$  was heated to 40° in a tube connected with a high vacuum pump (Found: loss, 6.25. Calc. for loss of 4 alc.: loss, 6.55%).

**Production of  $\alpha$ - $(AK)_6$ .**— $\alpha$ - $(AK,alc.)_6$  was left in a vacuum desiccator for 3 weeks (Found: K, 9.38.  $C_{120}H_{90}O_{24}S_{12}K_6$  requires K, 9.24%).

The substance was a thick gum, soluble in benzene. The solution in benzene was filtered into a little alcohol, and the resultant  $\alpha$ - $(AK,alc.)_6$ , 6alc. thrown out by the addition of light petroleum (b. p. 60–80°) [Found: K, 7.85; loss at 88°, 9.03. Calc. for  $\alpha$ - $(AK,alc.)_6$ , 6alc.: K, 7.59; loss of 1 alc., 8.95%].