45. *Molecular Compounds of Phenylacetic Acid and its Salts. Part I. A Covalent Compound of Sodium.*

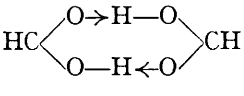
By Malcolm Crawford.

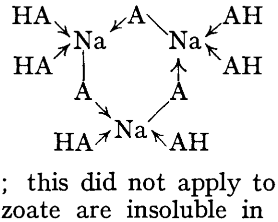
An acid " salt " of the composition NaA,2HA (A = $CH_2Ph·CO·O·$) has been prepared. Although it contains sodium, it is readily soluble in benzene and other organic solvents. The binary system NaA–HA has been studied, and molecular-weight determinations of the compounds have been made in various solvents. Acid sodium salts of benzoic and cinnamic acids, which, however, are not soluble in organic solvents, as well as other molecular compounds of sodium phenylacetate, have also been isolated.

It has long been known that many monobasic carboxylic acids form acid salts (for summary, see Ross and Morrison, J., 1933, 1016). Many of the acids themselves, such as benzoic, cinnamic, and phenylacetic, have been shown to exist as double molecules in solution (Pound and Pound, *J. Physical Chem.*, 1933, **37**, 971) and in the gaseous state. Pauling and Brockway (*Proc. Nat. Acad. Sci.*, 1924, **20**, 336) ascribe the structure (I) to formic acid vapour, but in order to account for the solubility in organic solvents it is assumed that the acid " salt " in question has a structure different from those of associated acids, in that it may not be held together by the hydrogen bond, but by co-ordination to a central metal atom, or, as is more likely from the molecular-weight determinations, to several metal atoms forming a polynuclear complex.

The majority of acid salts described in the literature are potassium salts, those of sodium being rarer. This is apparently only due to preparative difficulties, the sodium salts being generally more soluble and difficult to crystallise. Acid sodium *salts* have now been prepared from phenylacetic, benzoic, and cinnamic acids; the molar ratios of salt to acid for the first two acids respectively are 1 : 2 and 1 : 3, whereas the last acid forms derivatives of both types (phenylacetic acid may also form a 2 : 1 compound). Landrieu (*Compt. rend.*, 1920, **170**, 1452) has described an acid benzoate of the 1 : 2 composition, but this could not be confirmed. Both the cinnamates seemed to have a lower order of stability and their compositions altered on recrystallisation; this did not apply to the benzoate or phenylacetate. Both cinnamates and the benzoate are insoluble in most organic

(I.)





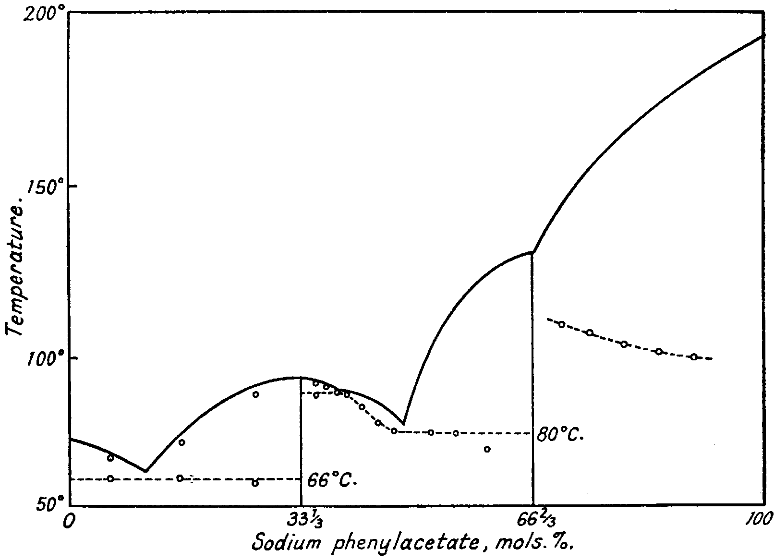
(II.)

solvents but soluble in aqueous and hydroxylic solvents such as hot water, acetic acid, glycerol, and phenol. When the hot aqueous solution is cooled, the acid separates. The phenylacetate, however, is a substance of entirely different character. It consists of fine hair-like threads, m. p. 94·4°. It is not salt-like and is readily soluble in benzene, ether, and chloroform; it is also water-soluble.

The solubility of this compound in organic solvents renders possible the determination of its molecular weight cryoscopically. Table I gives the results obtained with various solvents, M being the apparent molecular weight (calc., 430·2), and α the degree of association. There is a wide variation from solvent to solvent. In hydrocarbon solution α decreases with increasing temperature, which is to be expected from the flatness of the relevant portion of the curve representing the system acid–salt given in the figure. The compound is obviously considerably dissociated at its m. p. In the hydroxylic solvent dissociation into acid and salt is complete at ordinary temperatures, probably owing to combination of phenol with the salt, for an equimolar *compound* has been isolated and analysed. (Sodium phenylacetate forms a dihydrate but not an alcoholate, as far as can be ascertained.) In ketones there is no association of NaA,2HA as in hydrocarbons, which probably means that some sort of combination is taking place with the ketone. No compound with benzophenone could be isolated, but a probable *compound* of sodium phenylacetate with acetophenone has been obtained, although it is unstable.

TABLE I.

Solvent.	Approx. f. p. of solvent.	M.	α.	Solvent.	Approx. f.p. of solvent.	M.	α.
Benzene	5°	1390	3·2	Benzophenone ...	49°	458	1·1
Diphenylmethane	26	807	1·9	Camphor	176	300	0·7
Naphthalene	81	658	1·5	Phenol	42	171	0·4



The solubility and degree of association of sodium acid phenylacetate in hydrocarbons indicate that the sodium cannot be linked by electrovalencies, but by covalencies, and that there must be several sodium atoms in the molecule, forming a polynuclear co-ordination complex. Examples of alkali metals functioning as co-ordination centres are known but are rare. It is suggested that the simple formula $[NaA_3]H_2$ be replaced by a more complex one with perhaps three or more sodium atoms, such as (II), in which each sodium atom is assumed to be 4-covalent.

Ross and Morrison (*loc. cit.*) investigated the acid salts of mandelic acid, but were unable to study the binary systems acid–salt because of the instability of mandelic acid at and above its m. p.; they had to study the less satisfactory ternary systems acid–salt–water. These difficulties do not exist in the case of phenylacetic acid, and since sodium phenylacetate melts as low as 195° without decomposition except over long periods, the binary system has been examined by the determination of the m. p.'s of mixtures of the acid and salt. The results are given in Tables II and III and in the form of a diagram.

TABLE II.

Melting points of mixtures of acid and salt.

Salt, %.	M. p.	Salt, %.	M. p.	Salt, %.	M. p.	Salt, %.	M. p.	Salt, %.	M. p.	Salt, %.	M. p.
0·0	77·1°	27·0	92·3°	48·2	81·4°	64·6	128·9°	74·9	155·0°	89·0	180·1°
3·8	74·4	27·4	92·5	48·5	82·9	65·4	129·7	75·5	156·6	89·5	180·7
6·5	72·2	28·5	93·3	49·0	88·6	65·6	129·9	76·5	159·2	90·5	182·2
9·0	69·9	30·0	93·9	49·5	92·9	66·4	131·1	77·5	161·4	91·5	184·5
10·5	68·1	31·5	94·4	50·4	95·9	66·6	131·1	78·2	163·8	92·2	183·8
11·0	67·9	33·4	94·4	51·6	102·7	67·0	131·2	78·6	163·0	92·7	186·0
11·5	68·5	35·9	93·9	53·0	108·3	67·5	134·5	79·0	165·1	93·6	187·2
11·6	66·9	37·4	92·9	54·2	112·2	68·0	135·2	79·3	166·0	94·0	184·9
12·6	71·1	38·2	91·5	55·0	114·2	68·4	137·3	79·7	166·5	94·1	187·5
13·6	73·4	39·5	91·4	55·5	115·4	69·0	139·0	80·1	166·4	94·6	186·3
14·9	76·3	40·9	90·3	56·1	117·0	69·6	140·5	80·7	168·0	94·8	188·1
16·4	79·2	41·6	90·0	56·5	117·4	70·1	142·2	81·5	169·5	95·2	187·8
17·6	81·4	42·3	89·4	57·3	119·3	70·5	143·5	82·1	169·6	96·1	189·6
18·3	82·6	44·0	88·1	58·0	120·5	71·0	147·7	83·0	170·8	96·6	191·1
18·9	83·7	45·2	86·6	59·0	122·5	71·3	144·2	83·6	172·0	97·0	191·6
20·1	85·0	45·8	85·8	59·9	124·2	71·3	146·2	84·6	174·4	98·1	192·9
20·9	86·5	46·5	84·7	61·0	125·6	71·7	147·1	85·4	174·7	100·0	195·2
21·9	87·5	47·2	83·0	62·2	126·6	72·8	150·7	86·1	175·4		
24·0	90·0	47·4	81·6	62·9	127·4	73·9	153·3	86·9	177·6		
26·1	91·6	47·9	81·0	63·9	138·5	74·6	154·4	88·0	179·4		

Bakunin and Vitale (*Gazzetta*, 1935, **65**, 593) have already examined this system, but the results now obtained differ considerably from theirs; *e.g.*, they reported a third eutectic point between a compound of the composition HA,2NaA and NaA, whereas no eutectic depression is seen in the figure, and it is doubtful even whether this compound has a congruent m. p. Moreover, no compound of that composition could be isolated.

TABLE III.

Points of arrest in the cooling curves of mixtures of acid and salt.

Salt, %.	Liquidus arrest.	Solidus arrest.	Salt, %.	Liquidus arrest.	Solidus arrest.	Salt, %.	Liquidus arrest.	Solidus arrest.
5·9	72°	66°	41·9	—*	87°	64·8	—†	—
16·2	76	66	44·5	—*	82	71·0	—†	111°
26·9	90	65	46·5	—*	80	75·0	—†	108
35·5	93	90	48·0	—†	80	79·8	—†	105
37·0	—*	93	55·0	—†	79	85·0	—†	103
38·5	—*	91	59·9	—†	75	90·0	—†	102
40·0	—*	90						

* Only one arrest observed. † Liquidus arrest not determined.

The curve shows clearly the existence of the *compound* NaA,2HA and also two distinct eutectic points (67·5° at 11·1% of salt and 80·5° at 47·7% of salt).

The solidus portion of the diagram was determined by the cooling-curve method; hence with many mixtures the consequent supercooling and slow rate of crystallisation have caused many low results. In spite of this, the existence of the compounds NaA,2HA and HA,2NaA is substantiated. There is also strong evidence for the existence of a compound containing from 35 to 40% of salt. The liquidus line also shows some irregularity in this region. No such compound has been isolated, mixtures of this composition on recrystallisation invariably yielding NaA,2HA.

Mixtures of the composition HA,2NaA are not soluble in benzene or in other organic solvents, and recrystallisation from aqueous acetone or aqueous alcohol alters the composition. For this reason attempts to prepare a definite specimen of this compound failed.

EXPERIMENTAL.

The m. p.'s were determined upon about 0·5 g. of each mixture in an air-jacketed glass tube 3″ × 3/8″ in which a thermometer graduated in 0·5° was suspended, the whole being in a glycerol-bath of which the temperature could be raised or lowered extremely slowly. The cooling-curve method was not used owing to supercooling difficulties, it being possible to cool many of the mixtures to room temperature without crystallisation taking place. Instead, the m. p. was taken as the point at which, if a minute amount of the solid fused mixture were introduced on the tip of a glass needle with shaking, growth and not solution took place. In practice the needle was dipped into the fused liquid just above its m. p., withdrawn slightly above the liquid, allowed to cool sufficiently so that the drop of liquid solidified, and then reintroduced into the liquid. The growth or solution was observed through a lens. The m. p. so obtained proved to be identical within 0·1° with the point at which complete disappearance of crystals took place when the mixture, after fusion and solidification, was heated very slowly with agitation, a process requiring much more time. This simple method in which very small quantities were used gave remarkably consistent results, generally within 0·1°, except with certain mixtures, especially those in the vicinity of eutectic points, where increased viscosity reduced the rate of crystallisation.

Sodium Phenylacetate.—Concentrated aqueous sodium hydroxide was treated with a slight excess of alcoholic phenylacetic acid, and the mixture diluted with 10 vols. of alcohol, evaporated to small bulk, and diluted to the same volume with benzene. On concentrating, crystals separated which were recrystallised from slightly moist acetone. The resulting colourless needles of the dihydrate lose some water on standing in the air, and all of it quickly at 110°. The product is readily soluble in water or phenol, but only in alcohol and acetone after the addition of a trace of water [Found: *M* (cryoscopic in phenol), 144; (Rast method), 3300. Calc.: *M*, 158].

The Compound of Sodium Phenylacetate with Phenol.—Sodium carbonate ($\frac{1}{2}$ mol.) was added to a solution of phenylacetic acid (1 mol.) in phenol (2 mols.). The mixture was heated gently till all carbon dioxide had been evolved and was then allowed to cool. The solid mass was dissolved in carbon tetrachloride, and addition of light petroleum precipitated very hygroscopic needles, m. p. (in sealed tube) 105—125° (Found: PhOH, 36·8; $CH_2Ph{\cdot}CO_2H$, 53·8. $C_6H_5{\cdot}OH,C_6H_5{\cdot}CH_2{\cdot}CO_2Na$ requires PhOH, 37·3; $CH_2Ph{\cdot}CO_2H$, 54·0%).

The Compound of Sodium Phenylacetate with Acetophenone.—On cooling a hot solution of NaA in acetophenone, needles separated which were filtered off and dried on porous tile. The *substance* was decomposed into its constituents on treatment with water (Found: $CH_2Ph{\cdot}CO_2H$, 53·1; $CH_2Ph{\cdot}CO_2Na,C_6H_5{\cdot}CO{\cdot}CH_3$ requires $CH_2Ph{\cdot}CO_2H$, 48·9%). On recrystallisation from acetone, the substance lost acetophenone (Found: $CH_2Ph{\cdot}CO_2H$, 64·9%).

Sodium Acid Phenylacetate.—Sodium carbonate ($\frac{1}{2}$ mol.) was dissolved in a boiling benzene solution of phenylacetic acid (3 mols.). On concentration to small bulk and addition of excess of light petroleum, silky hair-like needles separated, which were recrystallised from benzene and light petroleum or from *cyclo*hexane, m. p. 94·4°, readily soluble in most organic solvents and in hot water (Found: $CH_2Ph{\cdot}CO_2H$, 63·1. $2C_8H_8O_2,C_8H_7O_2Na$ requires $C_8H_8O_2$, 63·2%). The values for the molecular weight of this *substance* given in Table I were determined by the Beckmann method, specially purified solvents being used.

Disodium Acid Phenylacetate.—NaA (2 mols.) and HA (1 mol.) were melted together and cooled, giving a crystalline mass. Powdered samples of this were insoluble in organic solvents, but soluble in moist acetone and in moist alcohol. The composition altered on recrystallisation from either of these, owing to loss of HA, becoming richer in NaA after each recrystallisation.

Possible Compound with 35—40% *of Sodium Phenylacetate.*—A mixture containing 40% of salt and 60% of acid was dissolved in benzene, and light petroleum added. The feathery crystals which separated after some time were found by titration to be pure NaA,2HA.

Sodium Acid Benzoate.—Sodium benzoate (1 mol.) was dissolved in the minimum amount of hot water, and benzoic acid (3 mols.) added together with sufficient acetone to dissolve it in hot solution. On cooling, needles separated which were recrystallised from acetone-water (5 : 1). The crystals melt at 227° in a sealed tube, and are insoluble in benzene, chloroform, or cold water. The solution in hot water deposits benzoic acid on cooling (Found: $C_6H_5{\cdot}CO_2H$, by titration, 70·4; Na, 4·5. $C_7H_5O_2Na,3C_7H_6O_2$ requires $C_6H_5{\cdot}CO_2H$, 71·7; Na, 4·5%).

Sodium Acid Cinnamates.—The two *compounds* were prepared by mixing solutions of cinnamic acid (2 and 3 mols. severally) in hot acetone with sodium carbonate (½ mol.) in hot water. More acetone was added when necessary till solution was complete. After some concentration, large needles separated on cooling (Found: $C_9H_8O_2$, by titration, 62·9, 72·8, respectively. $C_9H_7O_2Na,2C_9H_8O_2$ requires $C_9H_8O_2$, 63·5%. $C_9H_7O_2Na,3C_9H_8O_2$ requires $C_9H_8O_2$, 72·3%). When heated in a sealed capillary tube, the substances did not melt below 300°, but crystals, probably of cinnamic acid, sublimed. In both cases water dissolved out sodium cinnamate, leaving pure cinnamic acid.

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