589. *The Thermal Rearrangement of Alkali-metal Salicylates.*

By A. J. Rostron and A. M. Spivey.

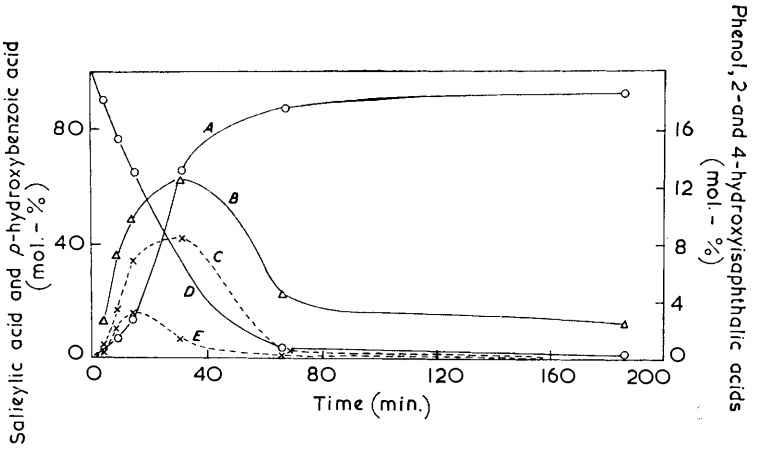
Mixtures of mono- and di-potassium salicylates give *p*-hydroxybenzoate on being heated between 207 and 240° in closed containers, initially sealed at low pressure. Salts of 2- and 4-hydroxyisophthalic acid and phenol appear to be intermediate products. Although only the dipotassium salt rearranges, mixtures containing 70% of the dipotassium salt yield *p*-hydroxybenzoate almost quantitatively whilst with mixtures containing 30% of dipotassium salt the rearrangement stops at somewhat lower conversions. Rearrangement occurs more readily under an increased pressure of carbon dioxide or nitrogen.

It has been recognised [1-4] that the rearrangement of alkali-metal salicylates to *p*-hydroxybenzoates is limited to the potassium, rubidium, and cæsium salts. The classical route [5] for the preparation of *p*-hydroxybenzoic acid involves heating monopotassium salicylate at 200—240°, 40% of the salicylate being converted into *p*-hydroxybenzoate whilst the remainder is recovered as phenol. In contrast, it has been claimed [6] that dipotassium

[1] Kolbe, *J. prakt. Chem.*, 1875, **11**, 85.
[2] Ost, *J. prakt. Chem.*, 1875, **11**, 385.
[3] Widequist, *Arkiv. Kemi*, 1954, **7**, 229.
[4] Hunt, Jones, Lindsey, Killoh, and Turner, *J.*, 1958, 3152.
[5] Buehler and Cate, *Org. Synth.*, Coll. Vol. II, 1943, p. 341.
[6] U.S.P. 1,937,477/1933.

salicylate rearranges almost quantitatively *in vacuo* or under a low pressure of carbon dioxide. Idris Jones and his co-workers [4] investigated the effect of heat on various alkali-metal salts of salicyclic and related acids. They suggested that the migrating group in this type of rearrangement, which could be inter- or intra-molecular, was $^{+}CO_2K$, and this was only loosely bound to the nucleus by a π-bond in the transition state.

We have investigated in greater detail the thermal rearrangement of mono- and di-potassium salicyclate and their mixtures, to *p*-hydroxybenzoates. In most of our experiments the dried salts were sealed at 0·01 mm. pressure into glass tubes which were then heated in an oil-bath at between 207 and 240°. For a given temperature, reaction was arrested at various stages by removing and cooling tubes at different times. The tube contents were then analysed for phenol and hydroxy-carboxylic acids, the latter by an ultraviolet spectral technique. The rearrangement was found to be very slow below 200 and quite rapid above 220°. Salts of 2- and 4-hydroxyisophthalic acids appeared transiently during reaction.

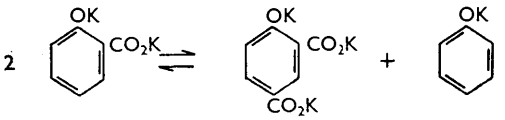


Rearrangement of dipotassium salicylate at 220°. (A) *p*-hydroxybenzoic acid; (B) phenol; (C) 4-hydroxyisophthalic acid; (D) salicyclic acid; (E) 2-hydroxyisophthalic acid.

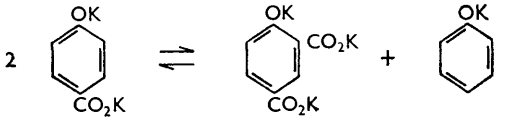
The Figure shows how the products varied with time during the rearrangement at 200° of dipotassium salicylate and is also typical of the rearrangement of mixtures containing 70 mol.-% of the di-salt. It will be noticed that the formation of *p*-hydroxybenzoate follows a sigmoid pattern as was observed by Idris Jones [4] and his co-workers who regarded it as typical of a solid-state autocatalytic reaction. These authors prepared very dry specimens of dipotassium salicylate and found no detectable rearrangement at 250°/0·1 mm. After they had exposed the salt to the atmosphere for a short time, rearrangement proceeded rapidly, *p*-hydroxybenzoate being the main product with traces of 4-hydroxyisophthalate and 6-hydroxytrimesate. We found the rearrangement of dipotassium salicylate to be even more rapid, 87 mol.-% having rearranged in 67 minutes at 220° compared with 5 mol.-% at 250° during 2 hours in their experiment.

A further examination of the Figure will show that, although the formation of *p*-hydroxybenzoate follows a sigmoid curve, the decomposition of salicyclic acid follows a logarithmic curve. This difference is not compatible with the rearrangement being a solid-state autocatalytic reaction with the migrating group being $^{+}CO_2K$ as the above authors suggested, but would be explained by the intermediate formation of salts of hydroxyisophthalic acid and phenol which we have observed. We suggest, on the basis of our results, that the reaction is intermolecular, proceeding through tripotassium 2- and 4-hydroxyisophthalates.

Equilibria (1) and (2), with similar equilibria embracing tripotassium 2-hydroxyisophthalate, would explain the formation and reconversion of these two salts and phenoxide. It is postulated that the equilibrium of reaction (1) is well to the right but the equilibrium



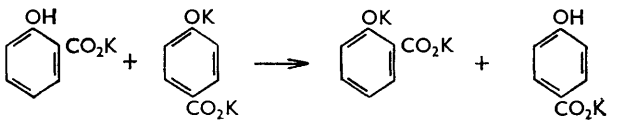
(1)



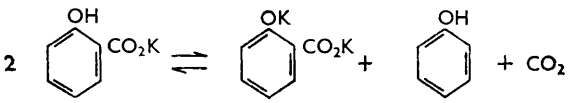
(2)

of reaction (2) is almost entirely to the left, so that hydroxyisophthalate and phenoxide ultimately react to form *p*-hydroxybenzoate.

At 220° a mixture of 70 mol.-% of di- and 30 mol.-% of mono-potassium salicylate gave approximately the same ultimate yield of *p*-hydroxybenzoate as the dipotassium salt although the time for 90 mol.-% conversion increased from 125 to 172 minutes. This indicates that the monopotassium salt at this concentration reacts, according to (3), with dipotassium *p*-hydroxybenzoate, already formed from dipotassium salicylate, to give dipotassium salicylate which will subsequently rearrange.



(3)



(4)

The phenol isolated from the rearranged products of monopotassium salicylate and a mixture of 70 mol.-% of mono- and 30 mol.-% of dipotassium salicylates at 220° was in excess of that equivalent to the 2- and 4-hydroxyisophthalate formed and the rearrangement ceased at 13 and 70—80 mol.-% conversions into *p*-hydroxybenzoate, respectively. It is postulated that part of the monopotassium salicylate in these salts decarboxylates according to reaction (4) as far as the equilibrium pressure will allow. Further evidence for this was the superatmospheric pressure found on opening the tubes. Nevertheless, the exchange reaction (3) must take place to some extent when monopotassium salicylate is heated under these conditions because the *p*-hydroxybenzoate yield is almost double that of the phenol yield.

Further experiments with other salts in sealed tubes showed that both mono- and disodium *p*-hydroxybenzoates were remarkably stable to heat for 3 hours at 220°, the small amount of phenol found probably resulting from traces of water in the salt. When sodium *p*-hydroxybenzoate and sodium phenate were heated at 220° for 3 hours, most of the former rearranged to sodium salicylate, with the formation of some phenol which again might have been due to the presence of water in the original salts. Heating disodium salicylate at 200° for 4 hours gave virtually no phenol, but sodium salicylate gave a 10 mol.-% yield of phenol, with no *p*-hydroxybenzoate in either case.

In experiments in an autoclave it has been demonstrated that the rearrangement occurs at a lower temperature under superatmospheric pressures of carbon dioxide or nitrogen. It is probable that increase of gas pressure enables the rearrangement to proceed at a

lower temperature by relaxing the chelate bonds as a result of penetrations by gas molecules. Widequist [3] has suggested that chelation is responsible for the failure of disodium salicylate to rearrange.

Experimental

Preparation of Metal Salts.—Approximately 65% solutions of the required salts were prepared from B.P. salicyclic acid and solutions of the requisite amounts of the appropriate analytical grade hydroxides. The bulk of the water was removed on the steam-bath under reduced pressure and the resulting viscous solutions were dried at 70° to a moisture content of 2—3% in an open dish on the steam-bath. The residue was finely ground and dried at 180—190° for 3 hr. at 15 mm. pressure of nitrogen with stirring. The moisture content of the salts was then 0·4—0·6%, as measured by the Karl Fischer method.[7] It was essential to add the Karl Fischer reagent to the solution of the sample in methanol otherwise high results were obtained, presumably because of reaction between iodine and easily hydrolysed alkali-metal salts.

Rearrangements of Salicylates.—For the small-scale rearrangements the dried salt (10 g.) was placed in a glass tube (100 mm. long, 15 mm. i.d.), which was evacuated to a pressure of 0·01 mm. Each tube was sealed, wrapped in stainless-steel gauze, and placed in an oil-bath stirred at the required temperature. After the requisite time the tubes were withdrawn, cooled, opened, and their contents treated as described below.

For the large scale rearrangements the finely ground dried salt (100 g.) was heated at the required temperature and pressure in a 1-l. mild-steel autoclave, fitted with a close fitting anchor-type stirrer.

Isolation and Analysis of Products.—After rearrangement the salts were dissolved in water as a 30% solution which was made alkaline with sodium hydroxide and buffered at pH 7—8 with borax. The solution was distilled in steam until phenol no longer distilled and the phenol in the distillate was determined by titration with standard bromate–bromide solution. The residue was acidified with 30% sulphuric acid and extracted continuously with ether. After evaporation of the ether the residue was dried at 60°, finely powdered, and analysed by a differential spectrometric method, the u.v. absorption of the sample being measured relative to that of pure salicylic acid with a Hilger " Unispek " spectrophotometer. Advantage was taken of the relative changes in the spectra of *p*-hydroxybenzoic acid and of 2-hydroxyisophthalic acid in passing from acidic (pH 2·8) to alkaline (pH 11·0) solutions which allowed a more accurate determination of these components. The shift in maxima of the u.v. spectra of *p*-hydroxybenzoic acid with changes in pH has already been reported by Doub and Vanderbelt.[8] Solutions were buffered at pH 2·8 with potassium hydrogen phthalate and hydrochloric acid and at pH 11·0 with disodium hydrogen phosphate and sodium hydroxide. Absorbance measurement at 350 mμ of the solution buffered at pH 2·8 allowed virtually direct determination of 2-hydroxyisophthalic acid whilst that of the solution buffered at pH 11·0 yielded values for *p*-hydroxybenzoic acid at 275 mμ, for 4-hydroxyisophthalic acid at 251 mμ, and for salicyclic acid at 295 mμ. The absorptivities of the components are given in Table 1. From the

Table 1.

Absorptivities of components.

Components		Absorptivity			
	Wavelength (mμ):	350	275	251	295
	Slit Width (mμ):	0·22	0·56	0·79	0·41
	pH:	2·8	11·0	11·0	11·0
2-Hydroxyisophthalic acid.....		*13·28*	4·18	7·30	19·97
p-Hydroxybenzoic acid		0	*121·2*	37·92	79·07
4-Hydroxyisophthalic acid.....		0·033	10·15	*51·39*	17·36
Salicylic acid		0·033	9·09	3·21	*25·55*

differential absorbances at the four key wavelengths and the absorptivities of the individual components, four simultaneous equations with four unknowns corresponding to the concentrations of 2- and 4-hydroxyisophthalic acids, *p*-hydroxybenzoic acid, and salicyclic acid may

[7] Wernimont and Hopkinson, *Ind. Eng. Chem., Analyt. Edn.*, 1943, **15**, 272.
[8] Doub and Vanderbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2721.

TABLE 2.

Rearrangements in sealed tubes.

Salt	Temp.	Time (min.)	Yield (mol.-%) 4-HIPA	2-HIPA	SA	pHBA	Phenol
Dipotassium salicylate	220°	4	0·8	0·5	90·3	3·1	2·5
	,,	9	3·4	2·0	76·9	7·9	7·3
	,,	14·5	6·8	2·9	64·5	14·8	9·7
	,,	31	8·4	1·4	7·1	64·2	12·6
	,,	67	0·7	0·3	3·3	87·3	4·2
	,,	186	0·1	0·1	0·3	92·8	2·2
70% Dipotassium salicylate	207	37·5	4·7	1·3	68·0	13·5	7·3
30% Monopotassium salicylate	,,	79	1·6	0·6	26·5	62·4	4·4
	,,	160	1·4	0·4	16·5	73·6	3·4
	,,	429	0·7	0·4	4·0	87·2	2·3
70% Dipotassium salicylate	220	35	5·0	3·0	47·2	27·7	14·1
30% Monopotassium salicylate	,,	68	1·9	0·6	16·3	72·8	3·8
	,,	128	0·3	0·4	2·8	88·0	2·7
	,,	216	0·4	0·2	0·4	92·3	2·1
	,,	480	0·4	0·1	0·4	91·8	1·7
70% Dipotassium salicylate	237	5	6·7	2·6	53·2	13·4	18
30% Monopotassium salicylate	,,	10·5	2·3	0·9	18·9	64·9	7·0
	,,	116	1·0	1·0	1·0	90·6	1·7
30% Dipotassium salicylate	220	27·5	0·2	0·3	61·8	31·1	3·5
70% Monopotassium salicylate	,,	52·5	0	0·6	56·1	33·9	3·9
	,,	64	0	0·6	44·1	45·6	4·0
	,,	165	0	0·7	21·6	64·4	7·2
Monopotassium salicylate	220	60	0·05	0·03	92·6	3·2	3·5
	,,	180	0·1	0·03	79·9	11·2	6·4
	,,	420	2·2	0·04	76·2	13·4	7·3
Disodium salicylate	220	240	0	0	99·5	0	1·4
	237	5·5	0	0	96·5	0	2·4
Monosodium salicylate	220	5	0	0	99·4	0	0·06
	,,	36	0	0	99·1	0	0·4
	,,	98	0	0	98·1	0	1·2
	,,	180	0	0	96·2	0	3·2
	,,	324	0·2	0·2	85·3	0·4	13·4
Monosodium *p*-hydroxybenzoate	207	182	0·1	0	0·4	94·9	2·9
Disodium *p*-hydroxybenzoate	220	182	0·5	0·1	0·5	94·5	3·3
0·35 mol. of monosodium *p*-hydroxybenzoate plus 0·65 mol. of sodium phenate	220	180	0·1	0	22·3	0·3	73

TABLE 3.

Rearrangements in the autoclave.

Salt	Temp.	Pressure (lbs./sq. in.)	Time (hr.)	Yields (mol.-%) 4-HIPA	2-HIPA	SA	p-HBA	Phenol
Dipotassium salicylate	160—183°	400—500 of nitrogen	8·5	1·5	0·2	0·3	83·9	5·6
Monosodium *p*-hydroxybenzoate	170—190	140—150 of carbon dioxide	6	0·7	0	4·0	87·1	1·6

be written and hence the concentration of these components determined. Analysis of a test mixture gave the following result:

	SA	pHBA	2-HIPA	4-HIPA
Present (%)	40·9	14·1	11·2	33·8
Found (%)	42·5	13·5	10·6	31·9

2-HIPA, 2-hydroxyisophthalic acid. SA, salicylic acid.
4-HIPA, 4-hydroxyisophthalic acid. pHBA, *p*-hydroxybenzoic acid.

The results of the rearrangements are given in Tables 2 and 3.

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