XXXVIII.—*On Nitro-Compounds.* Part II. Appendix.

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WHILE occupied with my experiments on nitrobenzoic acid, which have already appeared in the Society's Journal,* several minor questions presented themselves, all having reference to the main object of the inquiry, and to which I was anxious to obtain a response. One of these points, indeed, appeared of particular importance. I had met with various substances presenting differences in chemical behaviour, fusion-point, solubility, and general appearance, which agreed nevertheless in having the composition assigned to hydric mononitrobenzoate. It was very desirable that

* Chem. Soc. J. [2] iii, 319. To that place I refer for many details of preparation and properties necessarily omitted here.

these differences should become the subject of a special investigation. The results obtained are recorded in the following sections :—

1. *Alpha Hydric Nitrobenzoate*.—This substance, prepared by the action of absolute hydric nitrate on hydric benzoate and subsequent washing with water, was dried in air and afterwards at 100° C.

0·3520 grm. substance, gave 0·6492 grm. carbonic dioxide and 0·0949 grm. water.

	Found.	$C_7H_5NO_4$.
Carbon	50·30	50·30
Hydrogen.	2·99	2·99

The body was therefore pure. Its fusion-point* was next determined. The results were :—

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Fusion-point	129·9	139·2	136·4	135·2	133·8	133·8	136·7	133·0	125·7
Point of excessive heating	130	140	140	140	134	135	156	200	

The number in the second column was obtained after a very *slow* elevation of temperature. According to another determination, in a different apparatus, the first fusion-point was 127·5.

The original body was now converted into barytic salt by boiling with water and excess of pure barytic carbonate till the liquid lost its acid reaction. The solution was filtered off and allowed to cool, when an abundant deposit of white lustrous crystals occurred. These consist of thin flattened needles, sometimes of considerable length, and united together in radiated groups,—as if the individual crystals had once been parallel, but had been caused to diverge subsequently by some powerful constriction at the centre of the bundle. After standing in contact with the supernatant liquid for twenty hours, the latter was rapidly separated by filtration; and a known volume—100 cubic centimetres—evaporated to dryness on the water-bath, and dried at 150°. At that temperature the composition of the salt is represented by the formula

while the air-dried salt (at the ordinary temperature) contains, as is well known—

* All the fusion-points mentioned in this paper were taken with the same apparatus, except in a single case which is expressly alluded to. They are also all corrected in the usual manner. Substances were dried at 100° prior to fusion.

The crystals remaining on the filter were now again dissolved in about the same volume of water as previously, cooled, allowed to stand about twenty hours, and treated as before. Five consecutive determinations were made in this way. [The columns headed "solubility" show the number of parts of water required to dissolve one part of the salt.]

Crystallisation.	Temperature.	Solubility.	
		(Anhydrous).	(Hydrous).
(1)	6·6	431·3	375·5
(2)	8·6	425·1	370·0
(3)	8·8	456·7	397·6
(4)	10·0	469·6	408·8
(5)	8·8	745·6	414·0

The barytic salt remaining after this repeated crystallisation, was converted into hydric salt by treatment with hydric sulphate, washed and dried in air. It will be again referred to in Section 5.

α -Barytic nitrobenzoate preserves its appearance almost unchanged, even after exposure to the high temperature which has rendered it anhydrous. α -Hydric nitrobenzoate melts under water on very slight heating.

2. *Beta-Hydric Nitrobenzoate*.—This is the well-known modification obtained by the action of hydric nitrate upon toluol. In my last paper, owing to an inadvertence in the mode of experimenting, the solubility of this body was much underrated. I had used the process of evaporation, supposing the substance not to be volatile with the vapour of water at 100°—an error in which Zinin appears to have shared. The following numbers have been obtained in a more satisfactory manner:—

1. A solution saturated at 16° was neutralised with calcic carbonate, the calcium precipitated from the filtrate as oxalate, and this last dried and ignited after final moistening with hydric sulphate.

200 c. c. solution gave 0·0613 grm. calcic sulphate.

2. A solution saturated at 15°, was treated with barytic hydrate in excess, then with carbonic dioxide, and filtered. The filtrate was precipitated with hydric sulphate.

372·5 c. c. solution gave 0·1957 grm. barytic sulphate.

One part of this substance, accordingly, dissolves in—

I. 1327·1 parts of water at 16°.

II. 1326·5 parts of water at 15°.

Professor Abel very kindly sent me a small specimen of the hydric nitrobenzoate which he obtained* long since by the action of hydric nitrate on cumol. I purified this by boiling with chloride of lime, filtering the solution hot, and mixing the filtrate with hydric chloride. The crystals which separated on cooling were easily washed; they were then dried, ultimately at 100°, and fused. The fusion-point was 236·3. This number, owing to the mode of purifying employed, probably admits of comparison with that given for β -hydric nitrobenzoate by Willbrand and Beilstein—namely, 240°, a value which I have confirmed. The appearance of the substance is strikingly similar to that of the ordinary β variety; it also resembles the latter in the fact that it does not fuse under boiling water, and has a very slight solubility in cold water.

Zinin† and Sokoloff‡ have described a body, obtained by the action of hydric nitrate on desoxybenzoin, which they term “ β -nitrobenzoic acid,” and consider to be a new species. Zinin estimated its solubility at 1 in 1,200 parts of water at 17°, and remarks that it does not melt under boiling water. The fusion-point is not on record. Sokoloff states the solubility of his zinc salt (which crystallises in platy needles) to be 1 in 135 parts of water at the ordinary temperature, and expresses its composition by the formula

I have prepared the ordinary β -zinc salt, and find its description, so far as I can judge, to correspond with that of the body obtained by Zinin. A partial analysis and an approximate determination of its solubility are here appended.

0·4602 grm. substance, dried in the open air, gave 0·0864 grm. zinc oxide :

	Found.	$(\text{C}_7\text{H}_4\text{NO}_4)_2\text{Zn} + 2\text{H}_2\text{O}.$
Zinc	15·07	15·01

15 c. c. of a solution saturated at 17°, left 0·0943 grm. residue at 100°. [At this temperature the salt is probably anhydrous;

* Ann. Ch. Pharm. lxiii, 313.

† Ann. Ch. Pharm. cxxvi, 223.

‡ Bull. Imp. Acad. St. Pet., vii, 476.

heated further, it begins to decompose.] One part of this substance, therefore, calculated as hydrous salt, dissolves in 152·7 parts of water at 17°.

Sokoloff, who did not heat the residue, has probably given too low a result.

The potassic (β) nitrobenzoate, also, which I have prepared, resembles naphthalene.

3. *Gamma Hydric Nitrobenzoate*.—When hydric benzoate is digested for a short time at about 100° with the ordinary nitro-sulphuric mixture, there is produced, on adding water, a white precipitate differing from the two preceding bodies in certain particulars, but agreeing with them in composition. I distinguish it, provisionally, by the name which precedes this section.

The barytic salt was prepared in the manner already described, and the barium determined in a specimen dried in the open air.

0·5290 grm. gave, on evaporation with hydric sulphate and ignition, 0·2283 grm. barytic sulphate.

	Found.	$(C_7H_4NO_4)_2Ba + 4H_2O$.
Barium	25·37	25·32

Successive crystallisations and determinations of solubility were then resorted to, the latter being made on volumes varying from 30 to 150 c. c., and the residue dried at 150°.

Crystallisation.	Temperature.	Solubility.	
		(Anhydrous).	(Hydrous).
(3)	15·0	437·1	380·5
(4)	14·5	442·1	384·8
(5)	21·0	414·7	361·0
(6)	17·0	421·6	367·0

This salt can scarcely be said to be distinguishable in appearance from the α -nitrobenzoate. The mother-liquid of the second crystallisation was made to yield hydric salt as before, and this was submitted to fusion.

	(1)	(2)	(3)	(4)	(5)
Fusion-point	135·9	140·5	142·6	142·9	134·7
Point of excessive heating	136	141	153	153	—

The fusion-point of another preparation was 135·7. A specimen made from the sixth crystallisation of the barytic salt gave the consecutive numbers 132·5, 141·3. If the action of the nitro-

sulphuric mixture be continued for four hours the fusion-point of the nitrobenzoate so produced may be 141° .

The hydric salt melts easily under hot water.

Note.—The presence of a small quantity of hydric benzoate is well known to lower the fusion-point of hydric nitrobenzoate. Although I was satisfied by analysis that barytic benzoate was absent from the barytic salts I had prepared, or, at any rate, that its amount was perfectly inappreciable, it seemed that an estimation of the solubility of barytic benzoate might *possibly* not be without importance. The substance was prepared from sublimed hydric benzoate and pure barytic carbonate, and twice crystallised; the solution was neutral and saturated.

30 c. c. at $8^{\circ}3$ gave 0.8853 grm. barytic sulphate.

15 c. c. at $9^{\circ}1$ left 0.7225 grm. benzoate at 110° C.

1 part of the anhydrous salt, therefore, dissolves in—

20.83 parts of water at $8^{\circ}3$ C.

20.76 „ „ $9^{\circ}1$ C.

4. *Delta Hydric Nitrobenzoate.*—After the separation of the preceding hydric salt by means of water, the mother-liquid is allowed to repose for some time, filtered if necessary, and exactly precipitated by means of barytic carbonate, nitrate, or hydrate. On again filtering and evaporating to dryness, a residue is obtained, the amount of which is proportional to the length of the original digestion. It has the composition of hydric nitrobenzoate. It is best purified, first by pressure, then by conversion into barytic salt, which is washed with successive *small* quantities of cold water and crystallised. In this way a yellow colouring matter and some adhering hydric nitrate are removed. The hydric salt can be prepared in the usual way. It melts readily under hot water.

The barytic salt, made from hydric salt at the third crystallisation, was submitted to a partial analysis, after drying in the open air.

0.1718 grm., evaporated with hydric sulphate and ignited, gave 0.0747 grm. barytic sulphate.

	Found.	$(C_7H_4NO_4)_2Ba + 4H_2O$.
Barium	25.57	25.32

The solubility of this salt was as follows :—

45 c. c. of a solution saturated at $9^{\circ}7$ left 0.1266 grm. residue at 150° .

Accordingly, 1 part of the anhydrous salt dissolves
 in 359.3 parts of water
 1 part of the hydrous salt dissolves in
 309.3 parts of water } at $9^{\circ}7$.

Another preparation* of the barytic salt, after three crystallisations, was treated in the same manner.

0.3398 grms. gave 0.1456 grm. barytic sulphate.

	Found.	$(C_7H_4NO_4)_2Ba + 4H_2O$.
Barium	25.19	25.32

The determinations of solubility were made on 15—30 c. c. of solution.

Crystallisation.	Temperature.	Solubility.	
		(Anhydrous).	(Hydrous).
(5)	16	303.9	264.5
(6)	16	351.7	305.2
(7)	13	394.5	343.4

The above salt crystallises in forms much resembling those assumed by α and γ nitrobenzoate. The component crystals, however, of each group are much thicker and are terminated by less acute angles than in the other two cases; the groups themselves, also, are of relatively much smaller size.

The fusion-point of the hydric salt was determined on a specimen which had been thrice crystallised and was quite white.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Fusion-point	140.8	140.1	140.3	140.7	140.9	141.5	140.9	140.9	140.4	141.3
Point of excessive heating }	—	142	141	141	150	160	160	170	170	—

The first fusion-point has been confirmed by other determinations. The amount of crude substance originally obtained precludes the serious influence of any traces of the γ modification which might be supposed present.

(5). *Action of heat on α Hydric Nitrobenzoate and on Barytic Nitrobenzoates.*— α hydric nitrobenzoate, prepared from the barytic salt at the fifth crystallisation, was heated to 137° , and maintained at that temperature for a few minutes; it had fused

* For this specimen I am indebted to my friend Mr. John Ferguson.

long previously. After rapid cooling it was converted into barytic salt, and the solubility of this was determined.

30 c. c. of a solution saturated at $14^{\circ}5$ left 0.0913 grm. residue at 150° .

Accordingly, 1 part of the anhydrous salt dissolves
 in 328.5 parts of water }
 1 part of the hydrous salt dissolves in } at $14^{\circ}5$.
 286.9 parts of water }

γ and δ barytic nitrobenzoates change somewhat on heating to 150° . Residues from various determinations of the solubility of these salts were dissolved in water and crystallised; the mother-liquids contained bodies of greater solubility than the original nitrobenzoates, especially in the latter case.

(γ) 50 c. c. of a solution saturated at $19^{\circ}7$ left 0.1296 grm. residue at 150° . Solubility (of supposed anhydrous salt) 1 in 385.1 parts of water.

(δ) 15 c. c. of a solution saturated at 15° left 0.0784 grm. residue at 150° . Solubility (of anhydrous salt) 1 in 191.3 parts.

A yellow coloration accompanies this change. On the other hand, α barytic nitrobenzoate shows scarcely a sign of alteration under these circumstances.

Observations.

The experiments recorded in (1), (3), and (4), taken in connection with those described in my previous paper, show that there are bodies having the composition of hydric nitrobenzoate which melt at temperatures ranging from 128° to 141° . The disputed number (127°) given by Mulder is therefore confirmed, *although* the substance with which he worked was not free from hydric benzoate.

The fusion-point of these bodies evidently rises with the amount of force expended in their preparation; and their barytic derivatives decompose more easily the more preliminary work has been done upon them. When hydric nitrate is made to act upon hydric benzoate, the first nitrobenzoate obtained melts at about 128° . But, even here, if the action be considerably prolonged, the fusion-point may rise (as I had already shown) to 137.5° . Hydric benzoate (or the nitro-benzoate obtained by the first process) when treated with the ordinary nitro-sulphuric mixture for a short time, is transformed into a hydric nitro-benzoate fusing at

136°. Lastly, if this reaction be prolonged in its turn, a third nitrobenzoate is produced, melting at 141°.—Heat alone acts in a similar manner. It is shown in (1) that the fusion-point of the α -modification is much higher after the substance has been heated, and decidedly approximates towards that of the δ -modification. The same is true of the γ variety (3). Moreover the α nitrobenzoate, after a short and gentle fusion, yields a barytic salt which, in its solubility, strikingly accords with the δ -salt.

Naumann* has made some careful experiments on the fusion-point of hydric nitro-benzoate, which have led him to doubt Mulder's result. The bodies which yielded the number he mentions (141°) had, however, been submitted to repeated heating and a train of processes. A high fusion-point is precisely what might have been expected.

It will be noticed that the pure barytic salts (α and δ) are even unable to retain a constant solubility on repeated crystallisation; the γ -salt, on the other hand, exhibits a surprisingly perfect stability under the circumstances.

Such transformations under the influence of heat are already numerous and familiar. Those which are now recorded appear to resemble most closely, in the suddenness and minuteness of the effect, the corresponding changes observed by Duffy† in certain fats.

I will now compare the nitrobenzoates I have discussed.

α . The hydric salt melts first at about 128°. It yields a barytic derivative, which is but imperfectly stable on repeated crystallisation, less liable to decompose on heating than the α and γ barytic salts, more soluble than the γ salt, less soluble than the δ salt.

γ . The hydric salt melts first at about 136°. It yields a barytic derivative which is perfectly stable on repeated crystallisation, more liable to decompose on heating than the α -, but less so than the δ -salt; and less soluble than the α - or δ -salt.

δ . The hydric salt melts first at 141°. It yields a barytic derivative which is imperfectly stable on repeated crystallisation; more liable to decompose on heating than the α - or γ -salt; more soluble than those two bodies; and also different from them in that its crystalline groups are of smaller absolute size, and the individual crystals have less acute angles.

* Ann. Ch. Pharm. cxxxiii, 206.

† Chem. Soc. Qu. J. v. 179.

These differences find a parallel in the case of α - and β -lutidine described by Mr. Greville Williams*; and those bases also exhibit the striking resemblances which obtain among the above hydric nitrobenzoates.— β hydric nitrobenzoate is already well known as a definite species; it differs by the broadest characters from those which precede. I will only remark that it appears likely from (2) that the substance obtained by Abel, and that described by Zinin and Sokoloff are identical with what I had examined under the name " β -nitrobenzoic acid," and which had been termed "nitrodiaicylic acid" by other authors.

Finally, it will appear that the hydrogen in hydric benzoate is in such a condition that it is most minutely susceptible to the action of reagents. Three hydric chlorobenzoates are known,† in addition to the derivatives to which I have paid attention. We may legitimately suppose the most mobile of elements in the free state to preserve its character, to a certain extent, when combined; and in this respect, hydric benzoate only repeats on a more extensive scale what I have shown to be true for marsh-gas.‡

My best thanks are due to Professor Williamson for the use of his laboratory.