XLVII.—*On Nitro-Compounds* (Part II). *With Remarks on Isomerism.*

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THE experiments recorded in the preceding part* resulted in a classification of nitro-compounds according to their products of reduction, and in a contribution to the solution of the problem of the isomerism of the two nitranilines. The present part is chiefly devoted to the consideration of the two nitrobenzoic acids, and some general remarks are appended on the subject of isomerism itself.

(1) *Nitrobenzoic Acid.*

By the name *alpha*-nitrobenzoic acid I designate the solid product of the action of absolute nitric on ordinary benzoic acid. This is at present the only trustworthy process for obtaining it. The preparation is somewhat tedious, thorough nitration being effected only after eighteen hours boiling of the mixture, and nitric acid being repeatedly added to replace that which is lost by evaporation. After cooling and addition of water, nitrobenzoic acid separates out; it may be purified by continued washing with the precipitant.

The term *beta*-nitrobenzoic acid may be applied to that variety which was obtained by treating crude toluol with nitric acid, by Fischer† (who named it “*paranitrobenzoic acid*”) and Wilbrand and Beilstein‡ (who distinguished it as “*nitrodracrylic acid*”), and in all probability much earlier by Abel.§

β-Nitrobenzoic acid has been examined with considerable detail by several chemists, who have formed from it a large number of derivatives similar to, but not identical with, those derived from the sister compound. My object was to ascertain, if possible, the source of this difference. In preparing the second acid, Wilbrand and Beilstein’s method was followed precisely, with the exception of the final crystallisation from alcohol, which was found unnecessary. The fact that dinitrotoluol accompanies this body in large quantity is a very remarkable circumstance. The mem-

* Journ. Chem. Soc. [2] ii. 153.

† Ann. Ch. Pharm. cxxviii, 257.

‡ Ann. Ch. Pharm. cxxvii, 137.

§ Ann. Ch. Pharm. lxxiii, 313.

bers of the aromatic marsh-gas series, in fact, cannot be advanced to higher stages of nitration than the first without inducing a complicated reaction.

β -Nitrobenzoic acid differs in a most marked manner from the α -modification. The latter is said to dissolve in 400 parts of water* at 10° C.; the former, according to two determinations of my own, in 2,630 parts at 14° . The powder of the less soluble acid is highly electric. The formation of this substance may be approximately expressed by the following equation—

which was arrived at by weighing the first two of the specified products, correction being made for the solubility of the latter in the necessary washings.

	Found.		Theory.	
Dinitrotoluol	23·8821	gram.	5 mol.	84·49
β -Nitrobenzoic acid	4·2670	,,	1 mol.	15·51
	28·1491			100·00

Combustions and determinations of fusion-point were made both of the two nitrobenzoic acids and the dinitrotoluol, the results yielding very closely the well established numbers of recent observers.

The action of hydriodic acid on the two nitranilines, having borne fruit in some addition to our knowledge of the more intimate nature of those bases, very naturally suggested its extension to the two nitrobenzoic acids, which are immediately related to them. Experiment showed that boiling hydriodic acid of moderate strength produces the corresponding amidobenzoic hydriodates, with liberation of iodine. These salts may be obtained in tolerable purity by evaporating the liquid containing the products of the reaction to dryness, heating the residue to 100° as long as iodine continues to escape, dissolving in water, filtering, and crystallising. A small quantity of a brown substance removed in this process is probably due to the oxidising influence of free iodine.

* I find the acid to dissolve in 352·5 parts of water at 13° C. Higher numbers given by other authors probably refer to a substance obtained with the aid of sulphuric acid, and having a higher fusion-point than normal nitrobenzoic acid (128°).

The α -hydriodate dissolves easily in cold ether, alcohol, or hot water, crystallising readily from these solvents. It is a comparatively stable body.

The β -hydriodate dissolves less readily, and is soon coloured by exposure to air, especially if the temperature be raised.

Neither of these bodies produces a coloured reaction with argentic nitrate. The following iodine determinations were made:—

- (α) 0.5740 grm. substance, dried at 100°, gave 0.5145 grm. argentic iodide.
 (β) 0.4823 grm. substance, dried at 100°, gave 0.4218 grm. argentic iodide.

	Found.		Theory.
	α .	β .	$C_7H_5(H_2N)O_2.HI$.
Iodine	48.44	47.27	47.93

Hence the nitrobenzoic acids belong to the class of “amido-gens.”

In order to institute a comparison between the temperatures of attack of these substances by hydriodic acid, the same method was employed to which I have already alluded in Part I of these researches. I may be permitted to add here a brief description of the apparatus, which the accompanying figure will help to explain.

A beaker A, more than two-thirds filled with oil of vitriol, is adjusted on a ring-stand in the ordinary manner; its edge supports a thick cork, through the centre of which a hole is bored to admit the tube α , in which the reaction is to be performed. This tube contains a smaller one (the “weighing-tube,” in which the given substance is weighed), not shown in the figure, which is kept vertical by small beaks, or outward processes, from its edge. An

inclined position would interfere with the result. The tube *a* is furnished at its orifice with a cork having two apertures—one central, to admit a thermometer, and one lateral, to permit the escape of air and vapours. The thermometer is always brought to the same position previous to an experiment by reference to the stem of the ring-stand and any other convenient line, preferably vertical, in the vicinity. The tube B is placed at a suitable distance for observing the gradual obscuration, due to the free iodine, of the band of light occupying the proximate part of the cylindrical bulb of the thermometer. It is merely furnished, at *b*, with an upright glass thread to aid the eye in returning to the same position, and, on its upper part, with a spirit level. It admits of motion both vertically and horizontally. Both it and the ring-stand should be left unmoved throughout a series of observations. The operator's back is towards the light, and the experiments must be performed in the shadow of a partially opaque screen, to avoid the direct illumination of the beaker A. The bath of oil of vitriol in A has its surface on a level with that of the liquid in *a*. It should be heated uniformly, and with tolerable rapidity. The "attack-point" is the temperature at which the cylindrical portion of the bulb of the thermometer ceases to be visible.

The results thus procured show a remarkable difference between the nitrobenzoic acids—a difference greater even than that which obtains in like manner between the two nitranilines. The numbers are given in a table accompanying the present paper,* and curves are drawn to facilitate an immediate comparison. The necessary details of the apparatus, for which alone these results are here taken to hold good, are as follow :

Oil of vitriol in the bath	..	..	250 c.c.
Internal diameter of <i>a</i>	..	..	13.62 m.m.
Diameter of thermometer	..	..	3.80 "
Thickness of weighing tube	..	..	0.37 "
Hence width of obscured annulus	..	..	4.54 "
Volume of hydriodic acid employed	..	..	5.00 c.c.
Weight of substance taken	..	..	0.20 gm.
Rate of heating	..	..	1° in 11 seconds.

(2) *Action of Nitric on Benzoic Acid.*

The experiments of Wilbrand and Beilstein, already alluded to have shown that β -nitrobenzoic acid may be successively

* See opposite page.

transformed by known reactions into β -amidobenzoic, β -azo-amidobenzoic and benzoic acid. It was left an open question by those chemists whether the substance last produced was absolutely identical with ordinary benzoic acid, or different from it. The resemblance is, indeed, most remarkable. It has been already pointed out that in fusion-point, solubility in water and form of the calcium-salt*, there is no practical distinction between these bodies. I may add that their ethylic ethers are precisely alike in odour, a point on which frequent stress is laid in distinguishing isomeric substances. In order to decide this point, if possible, I submitted both ordinary benzoic acid and that derived from β -nitrobenzoic to the action of nitric acid, in the manner already described at the commencement of this paper. The liquid finally obtained was not precipitated with water, but evaporated to dryness at 100° . When the free nitric acid had completely volatilised, and the product had been allowed to cool, a gummy mass presented itself, in which crystals speedily made their appearance. The whole was transferred to a quantity of filter-paper, and heated to 100° for a few hours. White crystals were then found on the upper surface of the paper, while a very easily fusible substance had soaked down to its interior. The crystals are readily purified by means of alcohol, in which, as well as in ether, they rapidly dissolve in the cold; in boiling water they dissolve but sparingly;

CURVES ILLUSTRATING THE ATTACK OF ALPHA-NITROBENZOIC AND BETA-NITROBENZOIC ACID.

* Wilbrand and Beilstein, loc. cit.

in water at 15° scarcely at all. With caustic potash there is first a violet, and then a red coloration; but not solution, unless the liquid has been weak. These remarks, with the exception of the reaction just mentioned (which belongs to the derivative from the source β), apply equally to both bodies.

The fusion-point of the nitro-compound (from ? β -benzoic acid) was 201°·9 (cor.); its composition that of dinitrobenzoic acid.

0·2655 grm. substance, dried at 100°, gave 0·3802 grm. carbonic dioxide, and 0·0569 grm. water.

	Found.	Theory.
Carbon	39·05	39·62
Hydrogen	2·38	1·89

The readily fusible body occurring with this is extracted from the paper by ether, the solution filtered, evaporated to dryness, and the residue heated to 100° till constant. Thus prepared it probably contains a small quantity of the preceding compound, with which it agrees closely in its reactions; it is, however, more soluble in alcohol or ether. It melts at 88° (cor.), and scarcely solidifies on cooling.

0·37635 grm. substance, dried over oil of vitriol, gave 0·6044 grm. carbonic dioxide, and 0·1035 grm. water.

	Found.	Theory.	
		$C_7H_4(NO_2)_2O_2$	$C_7H_5(NO_2)O_2$
Carbon	43·79	39·62	50·30
Hydrogen	3·06	1·89	2·99

This product, therefore, is intermediate in composition between mono-nitrobenzoic and dinitrobenzoic acid, but decidedly approaches the latter.

The white crystals obtained from common benzoic acid, as mentioned above, melt at 137°·5 (cor.); after re-crystallisation from dilute nitric acid, washing, and drying, the fusion-point is 136°·3 (cor.)—a very slight alteration. They dissolve in 422·2 parts of water at 13°; and constitute, I believe, a definite compound.

0·3391 grm. substance, dried at 100°, gave 0·6225 grm. carbonic dioxide, and 0·1006 grm. water.

	Found.	Theory.
		$C_7H_5(NO_2)O_2$
Carbon	50·07	50·30
Hydrogen	3·29	2·99

Hence these crystals have the composition of *mononitrobenzoic acid*, but are not physically identical with it. I have not yet examined the more fusible body which accompanies them, and which appears to have hitherto escaped the notice of chemists.

The following experiments have a very important bearing on those just described :—

(3) *Simultaneous Action of Sulphuric and Nitric Acid on Ordinary Benzoic Acid.*

When benzoic acid is heated to 100° in a closed vessel with sulphuric and nitric acids, and the liquid cooled and mixed with water, a white crystalline precipitate falls, the yellow mother-liquid retaining in solution at least one other product. The nature of the result varies according to the time of digestion, and the quantity and strength of the mixed acids.

(1) *The precipitate.*—It is immaterial whether benzoic or α -nitrobenzoic acid has been used as the starting point. In either case, the product continues for some time to exhibit the composition of mononitrobenzoic acid, with an increased fusion-point and (it cannot be doubted) a decreased solubility. This fusion-point is always higher than 128°, provided the first stage of nitration has been reached.

One precipitate of this kind coincided remarkably with the white crystals last described in the preceding section. The substance fused at 136°·4 (cor.).

0·3225 grm. substance, dried at 100°, gave 0·5956 grm. carbonic dioxide and 0·0933 grm. water.

	Found.	Theory. $C_7H_5(NO_2)O_2$
Carbon	50·37	50·30
Hydrogen	3·21	2·99

If the action be continued beyond six hours, especially if absolute nitric acid be used, the nitration advances a stage further, and dinitrobenzoic acid is obtained. This appears to be a definite product, and has already been studied by Voit.* Neither his results nor my own, however, agree with those of Cahours; the time of preparation is not short, nor is the fusion-point of the

* Ann. Ch. Pharm. xcix, 100.

acid a low one. On the contrary, it melts at $206^{\circ}\cdot7$ (cor.) I may add also the following numbers :—

0·4196 grm. substance, dried at 100° , gave 0·6190 carbonic dioxide, and 0·0821 grm. water.

	Found.	Theory.
Carbon	40·23	39·62
Hydrogen	2·18	1·89

(2) *The mother-liquid*.—This is filtered from the precipitate, and the sulphuric acid it contains exactly removed by means of barytic hydrate, nitrate, or carbonate. The residual solution is evaporated to dryness, ultimately at 100° . The cooled crystalline mass, which is invariably coloured, yields a perfectly colourless product on extraction with carbonic disulphide. This body may be either *mononitrobenzoic acid*, or a mixture of that compound with small quantities of dinitrobenzoic acid.

The nitrobenzoic acid obtained in this way fused first at $127^{\circ}\cdot5$ (cor.) ; after cooling to solidification, it melted at $122^{\circ}\cdot4$ (cor.). Another preparation melted at $122^{\circ}\cdot3$ (cor.). It gives a red colouration with caustic potash.

0·3508 grm. substance, dried at 100° , gave 0·6393 grm. carbonic dioxide, and 0·1080 grm. water.

	Found.	Theory.
Carbon	49·70	50·30
Hydrogen	3·42	2·99

As an instance of the mixed result, I may adduce the following numbers :—

0·2812 grm. substance, dried at 100° , gave 0·4921 grm. carbonic dioxide, and 0·825 grm. water.

	Found.
Carbon	47·73
Hydrogen	3·26

(4) *Simultaneous Action of Sulphuric and Nitric Acid on β -Nitrobenzoic Acid.*

When the above named acids are heated together to a temperature of about 115° for several hours, cooled, and cautiously stirred with a moderate quantity of water, a precipitate falls after some

time. The yellow mother-liquid yields a second product on appropriate treatment. If the temperature of digestion be only 100° , only β -nitrobenzoic acid (with *unchanged* fusion-point) separates on the addition of water.

(1) *The precipitate*.—This has the composition of dinitrobenzoic acid. It dissolves very readily in cold alcohol or ether, and to a considerable extent in hot water. The solution is acid to litmus. With caustic potash it gives a beautiful red colouration. The fusion-point of one preparation was $161^{\circ}\cdot 9$ (cor.); after keeping several months, during which it was once heated on the water-bath for a few hours, the fusion-point was found to be $184^{\circ}\cdot 3$ (cor.) Another preparation gave the number $166^{\circ}\cdot 5$ (cor.).

0.2870 grm. substance, dried at 100° , gave 0.4207 grm. carbonic dioxide, and 0.0618 grm. water.

	Found.	Theory.
Carbon	39.98	39.62
Hydrogen	2.39	1.89

(2) *The mother-liquid*.—This was treated precisely as that mentioned in the preceding section. The product, however, having been found to be impure from calcium-salt, was mixed with a little water and primary potassic oxalate, dried, and extracted with ether. The latter solvent, on evaporation, left the body in a pure state, and almost free from colour. The substance melts at $153^{\circ}\cdot 1$ (cor.) to a clear liquid; dissolves with remarkable ease in cold alcohol or ether, but only slightly in water, and gives, with potash or ammonia, a beautiful deep red colouration. Rapidly heated alone, it explodes. After fusion it solidifies with extreme reluctance.

0.2920 grm. substance, dried over oil of vitriol, gave 0.4256 grm. carbonic dioxide, and 0.0697 water.

	Found.	Theory. $C_7H_5(NO_2)_2O_2$
Carbon	39.75	38.62
Hydrogen	2.65	1.89

This appears to be the only product remaining in the mother-liquid. Under the circumstances in which I examined it, it probably contained a small amount of the "*precipitate*."

(5). *General Observations.*

The remarkable difference between the temperatures at which α -nitrobenzoic and β -nitrobenzoic acid are attacked by hydriodic acid points clearly to a difference between the nitryl radicals they contain. This, it will be remembered, was the conclusion arrived at in the case of the two nitranilines, and it may doubtless be extended to many other isomeric nitro-compounds. Whether the nitryl of α -nitrobenzoic acid is, or is not, identical with that of α -nitraniline, is still an open question.

The experiments described in sections (2), (3), and (4) throw considerable light on the point they were intended to decide. It appears from (2)—though, from equal weights of the bodies not having been taken, the results are not absolutely precise—that benzoic acid prepared from gum benzoin is nitrated only with difficulty, whereas that obtained from β -nitrobenzoic acid is nitrated with remarkable ease. Under the circumstances mentioned, a mono-nitrocompound is obtained from the former, a di-nitrocompound from the latter. Now, if the resistance to nitration which ordinary benzoic acid manifests could be sharply overcome, it is clear that we ought to obtain β -nitrobenzoic acids from it. This condition is satisfied by the employment of a mixture of sulphuric and absolute nitric acid; a substance is produced having the composition of *di*-nitrobenzoic acid, and melting at $206^{\circ}7$. But benzoic acid derived from β -nitrobenzoic acid yields, to nitric acid alone, di-nitrobenzoic acid, melting at $201^{\circ}9$. This is as close an approximation as can be fairly expected. A further proof of the strong resistance which common benzoic acid presents to nitration is found in the contents of the mother-liquids obtained after digesting with sulphuric and nitric acid, and precipitating with water. That from α -nitrobenzoic acid contains altered α -nitrobenzoic acid; that from β -nitrobenzoic acid contains di-nitrobenzoic acid. On the whole, therefore, I consider that there are two species of benzoic acid. Gregory*, long since, observed the occurrence of two potassic benzoates. I intend to examine these interesting bodies still further, persuaded that they are the true sources of all the phenylic isomers.

* Ann. Ch. Pharm. lxxvii, 125.

(6). *Remarks on Isomerism.*

The great problem of isomerism, still pressing for solution, has hitherto been treated almost solely in accordance with atomic views. The statical theorists who have adopted these, and who suppose all bodies constituted of atoms fixed in space, hold that isomeric substances are produced by a variation of the *position* of some radical or radicals in the same molecule. The attempts to express this in formulæ, and the invention of a corresponding phraseology, are matters almost too familiar to require special notice. On the other hand, the principle of atomic motion—so largely accepted in physics, so little in chemistry—does not seem to have ever been considered available for speculations in this direction. There have been, however, partial indications of the attainment of a theory having no reference to corpuscular notions. Thus Graham* long since enunciated a peculiar doctrine of chemical action, and bestowed the names “zincous” and “chlorous” on the two opposite functions of one and the same element at the instant of disturbance. Brodie,† also, claimed for substances, at the moment of chemical change, a two-fold aspect or “polar” antithesis. Kekulé‡ and others pointed out that, in certain bodies containing replaceable hydrogen, one-half of this exhibits a different property from that shown by the other half; and they employed the terms “alcoholic” and “saline” to express the difference. Now these distinctions in *function*, considered as belonging to certain relative weights of known radicals, have no necessary connection with the doctrine of atoms, though frequently associated with it in ordinary scientific language.

Let us consider a special case of the phenomenon we are discussing. *a*-Nitrobenzoic acid is produced by the action of nitric upon benzoic acid from gum benzoin; *β*-nitrobenzoic acid results from the more complicated reaction between nitric acid and toluol, where oxidation as well as nitration takes place. Omitting, for the present, the oxidation observed in preparing the latter isomer, it is obvious that the difference in character whereby we distinguish two kinds of nitryl is conferred during the formation of the substances containing them. The nitryl of the nitric acid is of

* Elements (1842), p. 204.

† Phil. Trans. 1850, p. 762.

‡ Lehrbuch, vol. i. p. 130.

one nature; and this nature becomes altered in one or both cases of its transference. If, therefore, we would account for the alteration, we must do so by exploring further the reaction itself: in other words, it is a question of *force*.

That the functional change in nitryl does not depend wholly, by any means, on the composition of the residues with which it is associated, is clear from what we know of the nitranilines and nitrobenzoic acids. That it does not arise from what is termed the "satureability" of these residues is equally obvious. That nitryl influences and is influenced by the nature of what is combined with it is no doubt true to a certain extent; but if the properties of the nitranilines be compared in detail with those of the nitrobenzoic acids, it will become evident that the change alluded to has a logical claim to be considered a distinct phenomenon.

The numerous and remarkable oppositions furnished by isomerism, whether exhibited with respect to solubility, polarisation, fusion-point, basicity or the like, appear to present us only with the following principle of co-ordination,—that we may induce a *permanent* change in the properties of radicals by virtue of certain reactions. The formation of isomeric bodies, indeed, probably depends on precisely the same laws as that of bodies having differences of composition. The substitution of a radical with certain functions, for one with certain other functions but the same composition, differs only in this last respect from the exchange of a radical for one completely distinct; and, without reference to isomerism, it is easy to see that mere composition has a very subordinate bearing on the properties of a substance.

When we reflect that, of the radicals R , r , (having the same composition) we may have n R and m r simultaneously in a compound, where $n + m$ is a constant quantity, but where n and m may vary, the most complicated cases have a basis of classification. Thus, if the somewhat formidable array of the turpentine oils owe its number to the opposite natures which hydrogen is undoubtedly capable of assuming,* we should have here

$$n + m = 16;$$

and we might, of course, anticipate more isomers in this group than we are at present acquainted with. Again, with regard to

* For an instance of this see especially Hofmann on Hydra obenzol, Proc. Roy. Soc. xii, 578.

the hydric tartrates, of which there are three well-established species. If we conceive their isomerism to be also due to the functional difference of hydrogen, and that here

$$n + m = 2,$$

we at once account for their number and can deduce, from the small percentage value of the hydrogen concerned, that whatever difference there is must be very small. These, however, are merely hypotheses on two special cases; but I may remark with respect to the latter, that there is no evidence whatever to justify the common statement, that "inactive" hydric tartrate is a compound of the two "active" species, if it be meant that the last two have respectively half the molecular weight of the first.

The general formula of an isomeric group may be written as follows:—

$$(aA,ba) + (cB,db) + (eC,fc) + (gD,hd) + \text{etc.}$$

—A, a, &c., being the two opposite forms respectively of the ultimate component radicals; the italics representing their number, and being constant in sum for each of them.

The real problem of isomerism appears to be as follows:—*Under what conditions of action does chemical force induce a permanent alteration in one or more functions of radicals?* This I conceive to be the problem of every-day chemistry itself, which is occupied for the most part with the production of permanently different bodies.