

Citation:

A.F. Holleman & Huisinga, J., On the nitration of phthalic acid and isophthalic acid, in:
KNAW, Proceedings, 9 I, 1906, Amsterdam, 1906, pp. 286-292

Dinitrobenzoic acids	diss. const. at 40°	esterif. const at 40°
3.4	0 171	0.033
3.5	0 177	0.028
2.3	1 38	0.0025
2.5	2 16	0.0027
2.4	3.20	0 0017
2 6	7 6	< 0 0001

On perusing the literature we have found that this regularity does not exist in this series of dinitrobenzoic acids only, but is observed in a comparatively large number of cases. The strongest acids are the most slowly esterified. This might lead us to the conclusion that in the esterification by alcoholic hydrochloric acid it is not the ionised but the unsplit molecules of the acids which take part in the reaction.

A more detailed account of this investigation will appear in the *Recueil*.

Amsterdam }
Groningen } Sept. 1906; Laboratory of the University.

Chemistry. — Prof. HOLLEMAN presents a communication from himself and Dr. J. HUISINGA. "*On the nitration of phthalic acid and isophthalic acid*".

(Communicated in the meeting of September 29, 1906).

Of phthalic acid, two isomeric monoderivatives are possible, both of which are known particularly by a research of MILLER (A. 208, 233). Isophthalic acid can yield three isomeric mononitro-acids. Of these, the symmetric acid, which is yielded in the largest quantity during the nitration, is well known. As to the mononitrated by-products formed, the literature contains a difference of opinion; in any case, there is only made mention of one second mononitro-acid whose structure has remained doubtful.

The investigation of the nitration of phthalic and isophthalic acid was taken up by us in order to determine the relative amount of the isomers simultaneously formed, as in the case of the mononitro-

phthalic acids only a rough approximation (by MILLER) was known, whilst in the case of the mononitroisophthalic acids it had yet to be ascertained which isomers are formed there from.

We commenced by preparing the five mononitro-acids derived from phthalic acid and isophthalic acid in a perfectly pure condition. In the case of the α - and β -nitrophthalic acids no difficulties were encountered, as the directions of MILLER, save a few unimportant modifications, could be entirely followed. The acids were therefore obtained by nitration of phthalic acid and separation of the isomers.

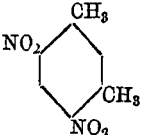
The *symmetric nitro-isophthalic acid* was prepared by nitration of isophthalic acid. It crystallises with 1 mol. of H_2O and melts at $255-256^\circ$ whilst it is stated in the literature that it crystallises with $1\frac{1}{2}$ mol. of H_2O and melts at 248° . At first we hoped that the other two nitroisophthalic acids might be obtained from the motherliquors of this acid. It was, therefore, necessary to obtain the isophthalic acid in a perfectly pure condition, as otherwise it would be doubtful whether the byproducts formed were really derived from isophthalic acid. By oxidation of pure *m*-xylene (from KAHLBAUM) an isophthalic acid was obtained which still contained terephthalic acid which could be removed by preparing the barium salts.

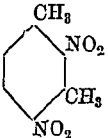
The motherliquors of the symmetric nitro-isophthalic acid appeared, however, to contain such a small quantity of the byproducts that the preparation of the nitro-acids (1, 3, 2) and (1, 3, 4) was out of the question. These were therefore, prepared as follows:

Preparation of asymmetric nitro-isophthalic acid (1, 3, 4). On cautious nitration of *m*-xylene at 0° with nitric acid of sp. gr. 1.48 a mixture is formed of mono- and dinitroxylene which still contains unchanged *m*-xylene. This, on distillation with water vapour, passes over first and when drops of the distillate begin to sink to the bottom of the receiver the latter is changed and the distillation is continued until crystals of dinitroxylene become visible in the condenser. 100 gr. of xylene gave about 85 gr. of mononitroxylol (1, 3, 4).

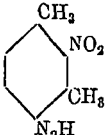
After rectification of this mononitroxylene (b. p. 238°) it was oxidised in alkaline solution with a slight excess of permanganate; 20 gr. yielded 12-à 13 gr. of acid which, however, consisted of a mixture of nitrotoluylic acid and nitro-isophthalic which could be separated by crystallisation from water. In this way, the as. nitro-isophthalic acid was obtained with a melting point of 245° . In water it is much more soluble than the symmetric acid, namely to the extent of about 1% at 25° . Unlike the symmetric acid, it crystallises without water of crystallisation in small, fairly thick, plate-like crystals. It is very readily soluble in hot water, alcohol and ether,

Preparation of the vicinal nitro-isophthalic acid (1, 3, 2). GREVINGK has observed that in the nitration of m-xylene with nitric and sulphuric acid

there is formed, besides the symmetric dinitro-m-xylene 

as main product, also the vicinal isomer . On reduction

with hydrogen sulphide both dinitroxylenes pass into nitro-xylidenes

which are comparatively easy to separate. The nitro-xylidene 

yields by elimination of the NH_2 -group vicinal nitro-m-xylene. Whilst however, GREVINGK states that he obtained a yield of 25% of vicinal nitroxylidene we have never obtained more than a few per cent of the same so that the preparation of vicinal nitro-m-xylene in this manner is a very tedious one, at least when large quantities are required. When it appeared that the "fabrique de produits chimiques de Thann et Mulhouse" exported this nitroxylene, the oxidation, although to some extent with material of our own manufacture, has been mainly carried out with the commercial product. This oxidation was also done with permanganate in alkaline solution. The vicinal nitro-isophthalic acid is a compound soluble with great difficulty in cold, but fairly soluble in hot water, crystallising in small beautiful, shining needles, which melt at 300° . It crystallises without any water of crystallisation and is readily soluble in alcohol and ether, from which it is again deposited in small needles.

The three possible mononitroisophthalic acids having now been obtained, we could take in hand the problem to ascertain the nature of the byproduct formed in the nitration of isophthalic acid. After the bulk of the nitroisophthalic acid formed had been removed by crystallisation, a residue was left which was far more soluble in water than this acid, which pointed to the presence of the asymmetric nitro-acid and which, indeed, could be separated by fractional crystallisation. We will see presently how it was ascertained that the nitration product was really only a mixture of the symmetric and the asymmetric acid.

As in the determination of the relative quantities in which the nitration products are formed, use was made of solubility determina

tions, we first give the solubilities in water at 25° of the five nitrophthalic acids, in parts per 100.

α -nitrophthalic acid	β -nitrophthalic acid
2.048	very soluble
symmetric nitroisophthalic acid	Asymmetric nitroisophthalic acid
with water of crystallisation.	0.967
0.157	
Vicinal nitroisophthalic acid	
0.216	

Quantitative nitration of phthalic acid. This was done with absolute nitric acid. It appeared that it proceeded very slowly even at 30°, and therefore the phthalic acid was left in contact with six times the quantity of nitric acid for three weeks. After dilution with water the acid was expelled by heating on a waterbath or else evaporated over burnt lime. The solid residue was then reduced to a fine powder and freed from the last traces of nitric acid by prolonged heating at 110°. As under the said circumstances the mononitrophthalic acids are not nitrated any further, it could be ascertained by titration whether all the phthalic acid had been converted into the mononitro-acid; the product had but a very slight yellow colour so that a contamination could be quite neglected. Of the product, now ready for analysis, different quantities were weighed and each time introduced into 100 c.c. of water, and after adding an excess of α -nitrophthalic acid they were placed in the shaking apparatus. The amount of acid dissolved was determined by titration and from these figures the content in β -acid was calculated by making use of a table which had been constructed previously and in which was indicated which β -nitroacid contents correspond with a definite titre of a solution so obtained. As the mean of four very concordant observations it was found that in the nitration of phthalic acid with absolute nitric acid at 30° is formed:

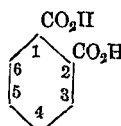
49.5 % α - and 50.5 % β -nitrophthalic acid.

The quantitative nitration of isophthalic acid was done in the same manner as that of phthalic acid; here also, a few weeks were required for the complete nitration at 30°. The contamination with yellow impurities could again be quite neglected as a but very faintly coloured nitration product was obtained. This nitration product so obtained contains the anhydrous symmetrical nitroisophthalic acid, so that in the solubility determinations by which its composition was determined the hydrated acid had to be employed as the anhydrous acid takes up water but very slowly and has a greater solubility. The

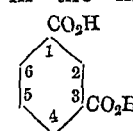
determination of the total amount of byproduct showed that this had formed to the extent of 3.1 % only. The qualitative investigation had shown already that this contains the asymmetric acid, and that it consists of this solely was proved in the following manner. If the 3.1 % found were indeed simply asymmetric acid, a solution, obtained by shaking 100 grams of water with excess of symmetric and vicinal acid, + 1 gram of nitration product (containing 0.031 gram of asymmetric acid), ought to have the same titre as a solution obtained by shaking 100 grams of water with excess of both acids + 0.031 gram of asymmetric acid. If on the other hand the nitration product also contained vicinal acid, therefore less than 0.031 gram of asymmetric acid, the titre ought to have been found less. This however, was not the case, which shows that the asymmetric acid is the sole byproduct. The result, therefore, is that in the nitration of isophthalic acid with absolute nitric acid at 30° there is formed:

96.9 % of symmetric and 3.1 % of asymmetric nitroisophthalic acid.

If we compare the above results with that of the nitration of benzoic acid where (at 30°) is formed 22.3 % ortho-, 76.5 % meta- and 1.2 % paranitrobenzoic acid the following is noticed.

As in phthalic acid  the positions 3 and 6 are meta in

regard to the one carboxyl and ortho in regard to the other and the positions 4 and 5 are also meta in regard to the one carboxyl but para in regard to the other it might be expected from my theories that the α -acid (the vicinal) is the main product and the β -acid the byproduct, because in the latter the nitro-group must be directed by one of the carboxyles towards para and because *p*-nitrobenzoic acid is formed only in very small quantity in the nitration of benzoic acid. As regards the isophthalic acid

 it might be expected that the chief product will be symmetric acid but that there will also be byproducts (1, 3, 2) and (1, 3, 4) the first in the largest quantity, although it should be remembered that a nitro-group seems to meet with great resistance if it must take a position between two other groups.

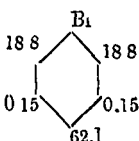
As regards the nitration of isophthalic acid the result of the above investigation is fairly satisfactory, although the total absence of the vicinal nitroisophthalic acid is somewhat remarkable. In the case of phthalic acid this is true in a less degree as about equal quantities are formed of the two possible isomers.

In his dissertation, Dr. HUISINGA has now endeavoured to calculate,

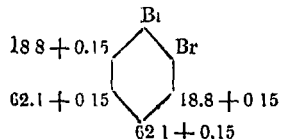
more accurately than before, from the relative proportion in which the isomers C_6H_4AC and C_6H_4BC are formed by the introduction of C in C_6H_5A or C_6H_5B , in what proportion the isomers C_6H_3ABC are formed by the introduction of C in C_6H_4AB . He observes first of all that in a substance C_6H_5A there are two ortho and two meta positions against one para position so that if the relation of the isomers is as C_6H_5AC $p : q : r$ (ortho, meta, para) this relation for each of the ortho and meta positions and for the para position will be $\frac{1}{2} p : \frac{1}{2} q : r$

He further gives the preference to an addition of these figures of proportion instead of a multiplication, which had been used by me up to the present in the prediction of these isomers. He prefers the addition because he considers the figures of proportion to be proportional to the directing forces which are exercised by the groups A and B on the other positions of the core and that the cooperation of such directing forces on one H-atom should be represented by a sum. But only the proportion of those directing forces are known and not their absolute value; the force which, in the nitration of nitrobenzene, pushes the NO_2 -group towards the *m*-position may be of quite a different order than the force which in the nitration of benzoic acid directs the same group towards the *m*-position. Therefore the figures which represent the directing forces (or are proportionate to the same) of two different groups cannot always be simply added together; this then will be permissible only when the two substituents present are equal.

As an example of his method of calculation the following may be mentioned. As in the nitration of bromobenzene 37.6% ortho, 62.1% para and 0.3% of meta nitrobenzene is formed, the substitution in the different positions of the benzene core takes place in the

proportion  ; for the proportion in which the isomers are

formed in the nitration of o-dibromobenzene the calculation gives

 or 62.25 : 18.95; or 76.7% asymmetric nitro-

o-dibromobenzene and 23.3% vicinal whilst the experiment gave 81.3% asymmetric and 18.3% vicinal.

It cannot be denied that in a number of cases this method of calculation gives figures which approach to the experimental ones a

good deal more than those obtained formerly when the undivided figures were simply multiplied. But on the other hand there are other cases, particularly those in which a metasubstituted substance is nitrated, where this calculation does not agree with the experiment by a long way. If we take into account the figures of proportion for the single positions we obtain as a rule a much better approach to the figures observed by means of the products than with the sums, even in the case where the two substituents present are unequal, when HUISINGA'S method of calculation cannot be applied. The proof thereof is laid down in the subjoined table which gives the figures of proportion in which the isomeric nitroderivatives are formed from the substances at the top of the columns, with the figures obtained from both the sums and the products.

	Cl:Cl ortho	Cl:Cl meta	Br:Br ortho	Br:Br meta	CO ₂ H:CO ₂ H ortho	CO ₂ H:CO ₂ H meta
found	7:93	4:96	18.3:81.7	4.6:95.4	49.5:50.5	3.1:96.9
product	18:82	9:91	23.3:76.7	13:87	82:18	*10.6:89.4
sum.	18:82	15:85	23.3:76.7	19:81	55.6:44.4	*38:62

*total quantity byproduct

	CO ₂ H:Cl ortho	CO ₂ H:Cl meta	CO ₂ H:Br ortho	CO ₂ H:Br meta
found	160:84.0	8.7:91.3	19.7:80.3	11.4:88.6
product	17.7:82.3	17.7:82.3	23.3:76.7	23.3:76.7

A fuller account of this investigation will appear in the *Recueil. Amsterdam, org. lab. Univ. 1906.*

Astronomy. — "*The relation between the spectra and the colours of the stars.*" By Dr. A. PANNEKOEK. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of September 29, 1906).

The close relation between a star's colour and its spectrum has long been known. The stars of the 1st, 2^d and 3^d types are usually called the white, the yellow and the red stars, although accurately spoken the colour of the so-called yellow stars is a very whitish unsaturated yellow colour and that of the so-called red stars is deep yellow mixed with very little red. In a paper read at Dusseldorf¹⁾ in

¹⁾ Die Farben der Gestirne. Mittheilungen der V. A. P. Jahrg. 10. S. 117.