

*Citation:*

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in the same manner, tetranitroresorcinol<sup>1)</sup> yields trinitrophenol; tetranitrochloro- and bromophenol also yield trinitrophenol on boiling with water or, more readily, with  $\text{Na}_2\text{CO}_3$  solution. By the action of  $\text{NH}_3$  or  $\text{NH}_2\text{C}_6\text{H}_5$ , etc. in alcoholic solution various other products are obtained, such as those substances included in the scheme which have been obtained previously from pentanitrophenol<sup>2)</sup>. We also see that water or alcohol cannot serve as a solvent for the purpose of recrystallising these compounds but that chloroform or carbon tetrachloride may be used.

If, in the above cited 3-5-substituted phenols the OH-group is substituted by  $\text{OCH}_3$ , it is not possible to introduce three nitro-groups. For instance the dimethylether of 5-nitroresorcinol yields two isomeric trinitroresorcinoldimethylethers (principally those with the melting point  $195^\circ$ , just as in the nitration of 5-nitro-m-xylene<sup>3)</sup>); similarly, the methylether of 5-nitro-m-cresol (m.p.  $70^\circ$ ) yields the methylethers of three isomeric trinitro-m-cresols, principally the compound with m.p.  $139^\circ$ . The constitution of these substances is not yet determined.

Amsterdam, September 1906.

**Chemistry.** — Prof. HOLLEMAN presents a communication from himself and Dr. H. A. SIRKS: "*The six isomeric dinitrobenzoic acids.*"

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

Complete sets of isomeric benzene derivatives  $\text{C}_6\text{H}_4\text{A}_2\text{B}$  have been studied but little up to the present; yet, for a closer understanding of those derivatives, it must be deemed of great importance to subject the six possible isomers of which such sets consist, to a comparative investigation. A contribution hereto is the investigation of the six isomeric dinitrobenzoic acids which Dr. SIRKS has executed under my directions.

The considerations which guided me in the choice of this series

<sup>1)</sup> According to HENRIQUES (Ann. Chem. 215, 335), tetranitroresorcinol (m.p.  $166^\circ$ ) is formed by the nitration of 2-5 dinitrophenol. In BEILSTEIN'S manual (vol. II, 926) a reasonable doubt is thrown on the correctness of this observation. The substance obtained has probably been an impure trinitroresorcinol formed by the action of water on the primary formed tetranitrophenol. (Rec. 21, 258).

<sup>2)</sup> Rec. 21, 264.

<sup>3)</sup> Rec. 25, 165.

of isomers were the following. Firstly, all six isomers were known, although the mode of preparation of some of them left much to be desired. Secondly, this series gave an opportunity to test V. MEYER'S "ester rule" with a much more extensive material than hitherto and to study what influence is exercised by the presence of two groups present in the different positions in the core, on the esterification velocity, and to compare this with that velocity in the monosubstituted benzoic acids. Thirdly, the dissociation constants of these acids could be subjected to a comparative research and their values connected with those of the esterification constants. Finally, the melting points and sp. gr. of the acids and their esters could be investigated in their relation to these same constants in other such series.

The six dinitrobenzoic acids were prepared as follows. The symmetric acid 1, 3, 5, (1 always indicates the position of the carboxyl group) was obtained by nitration of benzoic acid or of *m*-nitrobenzoic acid. All the others were prepared by oxidation of the corresponding dinitrotoluenes. This oxidation was carried out partly by permanganate in sulphuric acid solution, partly by prolonged boiling with nitric acid (sp. gr. 1.4) in a reflux apparatus.

We had to prepare ourselves three of the dinitrotoluenes, namely, (1,3,4), (1,3,6) and (1,3,2), ( $CH_3$  on 1); (1,2,4) and (1,2,6) are commercial articles whilst (1,3,5) was not wanted because the corresponding acid, as already stated, was readily accessible by direct nitration of benzoic acid. As will be seen the three dinitrotoluenes which had to be prepared are all derivatives of *m*-nitrotoluene and it was, therefore, tried which of those might be obtained by a further nitration of the same.

*m*-Nitrotoluene, which may now be obtained from DE HAEN in a pure condition and at a reasonable price was, therefore, treated with a mixture of nitric and sulphuric acids at 50°. On cooling the nitration-product a considerable amount of 1,3,4 dinitrotoluene crystallised out, which could be still further increased by fractionated distillation in vacuo of the liquid portion; the highest fractions always became solid and again yielded this dinitrotoluene, so that finally about 65 grms. of dinitrotoluene (1,3,4) were obtained from 100 grms. of *m*-nitrotoluene,

As the fractions with a lower boiling point, although almost free from dinitrotoluene (1,3,4), did not solidify on cooling, it was thought probable that they might contain, besides a little of the above dinitrotoluene, more than one of the other isomers, whose formation in the nitration of *m*-nitrotoluene is theoretically possible. If we consider

that, in the many cases which I have investigated, the presence of 1% of an isomer causes about 0.5° depression in the melting point, the fact that the oil did not solidify till considerably below 0° and again melted at a slight elevation of temperature whilst the pure isomers did not liquefy till 60° or above, cannot be explained by the presence of relatively small quantities of 1,3,4-dinitrotoluene in presence of *one* other constituent, but it must be supposed to consist of a ternary system. This was verified when the fractionation was continued still further; soon, the fractions with the lowest boiling points began to solidify on cooling, or slowly even at the ordinary temperature, and the solidified substance proved to be 1,2,3 — dinitrotoluene. The fractionation combined with the freezing of the different fractions then caused the isolation of a third isomer namely 1,3,6 — dinitrotoluene, so that the three isomeric dinitrotoluenes desired had thus all been obtained by the nitration of *m*-nitrotoluene. The fourth possible isomer (1,3,5) could not be observed even after continued fractionation and freezing.

As regards the relative quantities in which the three isomers, detected in the nitration product, are formed, it may be mentioned that this product consists of more than one half of 1, 3, 4-dinitrotoluene, whilst (1, 2, 3) seems to occur in larger quantities than (1, 3, 6), as the isolation of the latter in sufficient quantity gave the most trouble.

The *corrected solidifying points* of the dinitrotoluenes (the sixth, symmetric one was prepared by BEILSTEIN's method A. 158, 341 in order to complete the series) were determined as follows. Those of the dinitrobenzoic acids and of their ethyl esters are also included in the subjoined table.

	3.4	3.5	2.3	2.5	2.6	2.4
Dinitrotoluenes	58.3	92.6	59.3	50.2	65.2	70.1
Dinitrobenzoic acids	163.3	206.8	204.1	179.0	206.4	180.9
Ethyl esters	71.0	92.9	88.4	68.8	74.7	40.2

The *specific gravities* of the dinitrotoluenes and the ethyl esters were determined by means of EYKMAN's picnometer at 111°.0 with the following result:

$\left. \begin{array}{l} \text{CO}_2\text{H} \\ \text{or CH}_3 \end{array} \right\} \text{ on 1}$	toluenes	esters
3.4	1.2594	1.2791
3.5	1.2772	1.2935
2.3	1.2625	1.2825
2.5	1.2820	1.2859
2.4	1.2860	1.2858
2.6	1.2873	1.2923

Water at 4° as unity. Corrected for upward atmospheric pressure and for expansion of glass.

*Conductivity power.* This was determined in the usual manner with a Wheatstone-bridge and telephone at 25° and at 40°. As the acids are soluble in water with difficulty  $v = 100$  or 200 was taken as initial concentration; the end concentration was  $v = 800$  or 1600. In the subjoined table the dissociation constants are shown.

Dinitrobenzoic acid,	3.4	3.5	2.3	2.5	2.4	2.6
$K = 100k$ { at 25°	0.163	0.163	1.44	2.64	3.85	8.15
at 40°	0.171	0.177	1.38	2.16	3.20	7.57

On comparing these figures it is at once evident that the acids with ortho-placed nitro-group possess a much greater dissociation constant than the other two, so that in this respect, they may be divided into two groups. In the acids without an ortho-placed nitro-group, the value of the dissociation constant is fairly well the same. In the other four, the position of the second group seems to cause fairly large differences. That second group increases the said constant most when it is also placed ortho: in  $N/100$  solution 2-6-dinitrobenzoic acid is ionised already to the extent of 90%. Again, a  $\text{NO}_2$ -group in the para-position increases the dissociation constant more than one in the meta-position; and for the two acids 2,3 and 2,5 which both have the second group in the meta-position,  $K$  is considerably larger for 2,5, therefore for the non-vicinal acid than for the vicinal one, so that here an influence is exercised, not only by the position of the

groups in itself, but also by their position in regard to each other. It also follows that OSTWALD'S method for the calculation of the dissociation constants of disubstituted acids from those of the mono-substituted acids cannot be correct as is apparent from the subjoined table:

Dinitrobenzoic acid CO <sub>2</sub> H on 1	K calculated	K found
3.4	0.23	0.16
3.5	0.20	0.16
2.4	4.1	3.8
2.5	3.6	2.6
2.3	3.6	1.4
2.6	64	8.1

In the two vicinal acids 2,3 and 2,6 the deviations from the calculated value are particularly large, as I have previously shown for other vicinal substituted acids (Rec. 20, 363).

In view of the comparison of the figures for the dissociation constants of these acids and for their esterification constants, it seemed desirable to have also an opinion as to the molecular conductivity of these acids in alcoholic solution. They were, therefore dissolved in 95 vol. % alcohol to a N./<sub>200</sub> solution and the conductivity power of those liquids was determined at 25°. The subjoined table shows the values found and also those of the aqueous solutions of the same concentration and temperature :

dinitrobenzoic acids	3.4	3.5	2.3	2.5	2.6	2.4
$\mu_{260}$ in alcoh. sol.	1.1	1.15	1.75	2.25	2.7	2.9
$\mu_{200}$ in aqueous sol.	161.5	162.5	293	321	355.5	335.5

from which it appears that also in alcoholic solution the acids with an ortho-placed nitro-group are more ionised than the others.

*Esterification velocity.* The method followed was that of GOLDSCHMIDT, who dissolved the acid in a large excess of alcohol and used hydrochloric acid as catalyzer. The alcoholic hydrochloric acid used here

was 0.455 normal. Kept at the ordinary temperature it did not change its titre perceptibly for many months. As GOLDSCHMIDT showed that the constants are proportionate to the concentration of the catalyzer, they were all recalculated to a concentration of normal hydrochloric acid. Owing to the large excess of alcohol the equation for unimolecular reaction could be applied. The velocity measurements were executed at 25°, 40° and 50°. At these last two temperatures, the titre of the alcoholic acid very slowly receded (formation of ethylchloride) and a correction had, therefore, to be applied. The strength of the alcohol used was 98.2 % by volume.

In order to be able to compare not only the esterification-constants *E* of the dinitrobenzoic acids with each other but also with those of benzoic acid and its mononitroderivatives, the constants for those acids were determined at 25° under exactly the same circumstances as in the case of the dinitroacids. The results obtained are shown in the subjoined table :

Acids	E at 25°	E at 40°	E at 50°
benzoic acid	0.0132	—	—
m. NO <sub>2</sub> »	0.0071	—	—
o. » »	0.0010	—	—
3.4 dinitro »	0.0086	0.033	0.077
3.5 » »	0.0053	0.028	0.060
2.3 » »	0.0005	0.0025	0.0071
2.5 » »	0.0003	0.0027	0.0076
2.4 » »	0.0002	0.0017	0.0056
2.6 » »	unmeasurably small		

As will be seen, *E* is by far the largest for benzoic acid and each subsequent substitution decreases its value.

On perusing this table it is at once evident that in the dinitrobenzoic acids two groups can be distinguished. Those with an ortho-placed nitro-group have a much *smaller* constant than the other two. *Whilst therefore the dissociation constant for acids with an ortho-placed nitro-group is the largest their esterification constant is the smallest.* As shown from the subjoined table, this phenomenon proceeds quite parallel; the acids whose dissociation constant is greatest have the smallest esterification constant and vice versa.

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*.

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

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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-