

Citation:

A.F. Holleman, The quantitative estimation of the products of nitration of m-chloro and m-bromobenzoic acid., in:

KNAW, Proceedings, 11, 1908-1909, Amsterdam, 1909, pp. 260-266

temperature higher substituted nitro-products were readily formed.

If the nitration is carried out at $+60^{\circ}$ a product is formed which solidifies at $-9^{\circ},2$, a temperature which is situated lower than the eutectic one of mixtures of the two pure components. The sp. gr. is 1.2626. No doubt considerable quantities of polyvalent nitro-compounds are formed at this high temperature of nitration.

Amsterdam, Org. chem. lab. Univ. Aug. '08.

Chemistry. — "*The quantitative estimation of the products of nitration of m-chloro and m-bromobenzoic acid.* By Prof. A. F. HOLLEMAN.

The above investigation has occupied me more than once.¹⁾ In the nitration of each of these acids two nitrohalogen acids are formed namely 1,6,3 = $\text{CO}_2\text{H}, \text{NO}_2, \text{Cl}(\text{Br})$ as main product and 1,2,3 = $\text{CO}_2\text{H}, \text{NO}_2, \text{Cl}(\text{Br})$ as byproduct; the question arose in what proportion these acids are present in the nitration mixture.

The reasons which induced me to revert to this investigation are twofold. Firstly, because the percentage of byproduct in the nitration mixture of *m*-chlorobenzoic acid was found 2.8 higher in the first investigation than in the second, when another method of analysis was applied and this difference was not satisfactorily explained. Secondly because it was found in the nitration of *o*-chloro- and *o*-bromobenzoic acid and also in that of *m*-chlorobenzoic acid, that more byproduct is formed at 0° than at -30° , whereas in the nitration of *m*-bromobenzoic acid the very opposite result was noticed.

In the first investigation the quantity of main product was determined by extracting the nitration mixture with benzene and determining the sp. gr. of the benzene solution. In the second determination the quantity of byproduct was deduced from the solidifying point of the mixture. A third *modus operandi* was followed for this renewed investigation, namely, the extraction of the nitration mixture with water and titration of the aqueous solution obtained.

I do not intend giving any further details of these methods as I described these repeatedly on former occasions.

Mssrs. J. J. POLAK and H. L. DE LEEUW, who have carried out these investigations independently, started from chemically pure preparations of *m*-chloro- and *m*-bromobenzoic acid, which were nitrated with absolute nitric acid after which the nitration product was collected according

¹⁾ R. 19 188, [1900] and R. 20, 223 [1908].

to the method given in *R.* 20, 223. I will only add that the complete removal of nitric acid from the product was effected with particular care as it appeared that this acid is retained with great obstinacy. In order to get the nitration product so pure that it gave, at the ordinary temperature, no, or but a feeble reaction with sulphuric acid and diphenylamine, it was necessary to wash it many times with cold water and to dry it over lime in vacuo. The organic acids, which had dissolved in the washings were, of course, recovered in the manner described previously. The removal of the last traces of nitric acid was of great importance in these determinations, because the presence of even very minute quantities of this acid causes, in the analytical method followed here, a too low percentage of the byproduct.

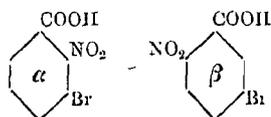
In this method about 0.4 gram of nitration mixture is extracted with 100 grams of water and the acidity estimated by titration with $\frac{1}{10}$ alkali. Suppose 1 mgr. of nitric acid ($= 0.25\%$) had been retained in that quantity it is sure to have dissolved together with the whole of the main product. 1 mgr. $= 0.016$ millimol. 1 cm.³ of the alkali corresponds with 0.1 millimol. so that 0.16 cm.³ or about 3 drops are required for neutralisation. As the molecular weight of chloronitrobenzoic acid is 201.5 and that of bromonitrobenzoic acid 246, 0.016 millimol. represents, respectively, a weight of 3.2 and 3.9 mgr. or of $\frac{1}{4}\%$ and 1% of the nitration mixture. The main product contained therein is therefore found too high and the byproduct correspondingly too low since the latter is found by difference. As the content in byproduct in these mixtures does not exceed 13% (in the bromo-acids) an error of 1% is a rather serious one.

In order to be able to determine the composition of the nitration mixtures by solubility determinations it was necessary to determine first for the chloro- and bromobenzoic acids, the solubility of the least soluble ones (in both cases the byproduct) and then the total solubility, when the liquid is kept saturated with this least soluble acid, but mixed with gradually increasing portions of the main product; when the liquid does not get saturated, all the main product passes into solution. By means of the solubility tables thus obtained the composition of an unknown mixture may be deduced reversedly by determining its solubility figure.

SOLUBILITY LINES.

Temperature 25.°0.

1. Bromonitrobenzoic acids



MW 246

Quantity of substance shaken with 100 cc. of water	Pipetted off	cc. of alkali (0.0287 <i>n</i>)	Total solubility in grams per 100 cc. of solution
100 mgrs. α	59.455 grs.	2.75	0.033
1 gram β	60.180 „	63.15	0.741
100mgrs. α + 118.8mgrs. β	26.211 „	5.00	0.135
„ + 203.7 „ „	32.345 „	9.90	0.216
„ + 299.0 „ „	31.050 „	13.60	0.309
„ + 402.0 „ „	19.021 „	11.00	0.408
„ + 497.6 „ „	20.176 „	15.65	0.502
„ + 587.3 „ „	20.337 „	17.05	0.592

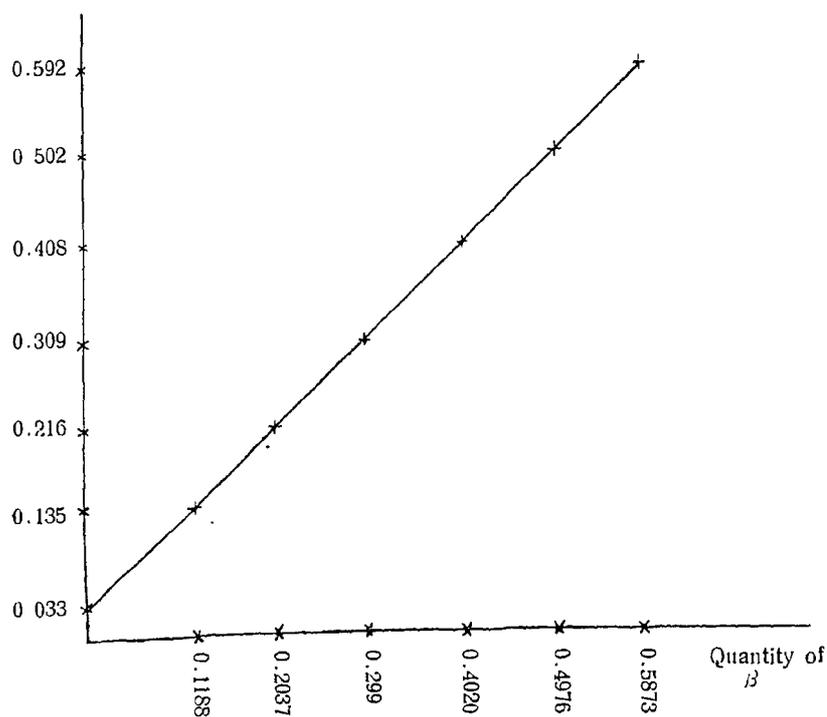
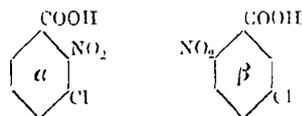


Fig. 1. Total solubility of mixtures of the bromonitrobenzoic acids constructed according to the table.

Duplicate determinations made by again titrating an aliquot portion from the bottles gave results within the limit of experimental error.

The graphic representation Fig. 1 shows that the line, except for a small deviation at the start, is a straight one.

2. Chloronitrobenzoic acids.



Temp. 25.5° MW 201.5.

Quantity of substance shaken with 100 cc. of water	Pipetted off	cc of alkali (0.0295 <i>n</i>)	Total solubility in grams per 100 cc. of solution
150 mgrs. α	37.611 grs.	3.0 cc.	0.047
1 gr. β	18.378 „	29.20	0.967
100 mgrs. $\alpha + 0.3020 \beta$	29.650 „	15.70	0.315
100 mgrs. $\alpha + 0.4120 \beta$	23.240 „	16.35	0.418

These titrations are accurate within 2 drops of 0.03 normal alkali. As this corresponds with about 0.7 mgr. of chloro- and 0.8 mgr. of bromonitrobenzoic acid the last figure of the numbers of the last column may be about one unit wrong. The tables have been constructed by Mr. POTAK.

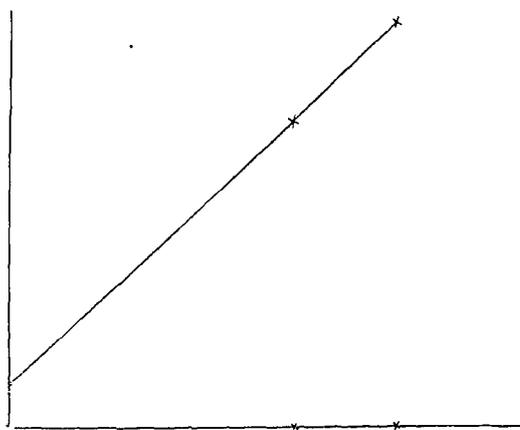


Fig. 2. Total solubility of mixtures of the chloronitrobenzoic acids, constructed according to the table.

As may be seen from fig. 2, the line is practically a straight one.

The nitrations of *m*-chloro- and *m*-bromobenzoic acid were carried out in the approved manner by means of absolute nitric acid at 0° and at -30° In order to ascertain whether all had been converted into mononitro-acids the molecular weight of the products formed

was determined by titration. For this purpose 0.1 gram of the nitration mixture was dissolved in water and titrated with N/10 alkali; when using phenolphthaleine as indicator this titration is accurate within one drop. 0.1 gram is about 0.5 millimol of chloro- and 0.4 millimol of bromonitrobenzoic acid which require 5 and 4 cc. of N/10 alkali respectively. One drop (0.05 cc.) corresponds therefore, with 1% of the molecular weight of the chloro- or 0.8% of the bromo-acid. If now the molecular weight lies between 201.5 ± 2 or 246 ± 2 , respectively the substance may be taken to be pure nitro-acid. True it might be possible that, accidentally, a mixture had formed consisting of unattacked acid, mononitro- and dinitro-acid, which apparently possesses the molecular weight of the pure mononitro-acid but apart from the improbability that this should have formed, the possibility was also excluded, because the nitration mixture of *m*-bromobenzoic acid was again treated with absolute nitric-acid, which caused no serious alteration in the molecular weight. Mol. weight first 245; on repeated treatment 247.

Mr. DE LEEUW obtained the following results in the analysis of the nitration products prepared by himself.

I. Nitration of *m*-chlorobenzoic acid at 0°; 5 grams treated with 30 grams of absolute nitric acid.

Mol. weight of the product 203.2.

1. Weighed 381.9 mgrs. of nitration product; shaken with about 100 mgrs. of byproduct ($CO_2, H, Cl, NO_2 = 1, 3, 2$) and 100 grams of water at 25°.

Pipetted off 36.256 grams of solution which required 15.10 cc. of 0.0432 normal potassium hydroxide for neutralisation.

Main product 92.4%; byproduct 7.6%.

2. Weighed 364.1 mgrs. of nitration product; shaken with about 100 mgrs. of byproduct and 100 grams of water at 25°.

Pipetted off 69.464 grams which required 27.85 cc. of the said alkali for neutralisation.

Main product 92.8%; byproduct 7.2%.

II. Nitration of *m*-chlorobenzoic acid at -30°; 5 grams treated with 30 grams of absolute nitric acid.

Molecular weight of the nitration product 200.4.

1. Weighed 351.7 mgrs. of the product; shaken with about 100 mgrs. of byproduct and 100 grams of water at 25°. Pipetted off 34.538 grams of solution which required 13.5 cc. of the above alkali for neutralisation.

Main product 93.5%; byproduct 6.5%.

2. 372.8 mgrs. treated as directed; Pipetted off 35.448 grams of solution which required 14.51 cc. of alkali for neutralisation.

Main product 92.8%; byproduct 7.2%.

III. Nitration of *m*-bromobenzoic acid at 0°.

5 grams treated with 30 grams of absolute nitric acid.

Mol. weight of the nitration product 243.7.

Weighed 424.0 mgrs. of the product; shaken with 100 mgrs. of byproduct and 100 grams of water at 25°. Pipetted off 33.945 grams which required 12.19 cc. of alkali for neutralisation.

Main product 88.3%; byproduct 11.7%.

IV. Nitration of *m*-bromobenzoic acid at -30°.

Mol. weight 243.4.

374.4 mgrs. treated as directed. Pipetted off 31.661 grams of liquid which required 9.91 cc. of alkali for neutralisation.

Main product 88.6%; byproduct 11.4%.

Mr. POLAK has repeated these investigations with great care in which he used material prepared by himself. In order to be sure that the nitration products did not retain any nitric acid they were analysed in the manner described, after the test with diphenylamine had become negative. The remainder of the preparation was then again triturated and washed with cold water; the dissolved organic acids were recovered from the washings and the preparation thus purified was again submitted to analysis. The two analyses are indicated with I and II.

Cl 0°. M.W. 202.9 (201.5).

I 0.3374 gr. of nit. mixture +100 mgr. of <i>z</i> in 100 cc.	94.333 gr. of sol. β 0.3104	16.39 cc. of (0.0922) <i>n</i> alkali β 92.9%	Tot. sol. 0.328 <i>z</i> 8.0%
II 0.3315 gr. of nit. mixture +100 mgr. of <i>z</i> in 100 cc.	45.516 gr. of sol. β 0.3053	7.28 cc. of (0.0922) <i>n</i> alkali β 92.1%	Tot. sol. 0.3180 <i>z</i> = 7.9%

Cl-30° M.W. 203.3 (201.5).

I 0.3410 gr. of nitr. mixture	98.157 gr. of sol. β : 0.3181	17.43 cc. of (0.0922) <i>n</i> alkali β = 93.3%	Tot. sol. 0.3300 <i>z</i> : 6.7%
II 0.3275 gr. of nitr. mixture	66.284 gr. of sol. β 0.3063	11.40 cc. of (0.0922) <i>n</i> alkali β = 93.7%	Tot. sol. 0.3195 <i>z</i> : 6.3%

Br 0° M.W. 245.7 (246).

I 0.3320 gr. of nitr. mixture	55.477 gr. of sol. β 0.2898	7.32 cc. of (0.0922) <i>n</i> alkali β = 87.0%	Tot. sol. 0.2993 <i>z</i> : 13.0%
II 0.3292 gr. of nitr. mixture	67.915 gr. of sol. β 0.2868	8.96 cc. of (0.0922) <i>n</i> alkali β = 87.1%	Tot. sol. 0.2971 <i>z</i> = 12.9%

Br. -30°. M.W. 245.2 (246).

I 0.4585 gr. of nitr. mixture	89.965 gr. of sol. β = 0.4096	16.48 cc. of (0.0922) <i>n</i> alkali β : 89.3%	Tot. sol. 0.4155 <i>z</i> : 10.7%
II 0.4385 gr. of nitr. mixture	64.190 gr. of sol. β : 0.3192	11.20 cc. of (0.0922) <i>n</i> alkali β : 89.2%	Tot. sol. 0.3957 <i>z</i> : 10.8%

Let us now include all the figures obtained in the subjoined tables.

I. Nitration of *m*-chlorobenzoic acid; % of byproduct in the nitration mixture.

	DE LEEUW			POLAK			HOLLEMAN, R.20,206		
	%	mol. weight		%	mol. weight		%	mol. weight	
Temp. 0°.	7.6	7.2	203.2	8.0	7.9	202.9	8.7	202.5	calculated
Temp.—30°.	6.5	7.2	200.4	6.7	6.3	203.8	8.3	201.5	201.5

II. Nitration of *m*-bromobenzoic acid.

Temp. 0°.	11.7	243.7	13.0	12.9	245.7	11.4	245	mol. weight calculated
Temp.—30°.	11.4	243.4	10.7	10.8	245.2	11.8	243.2	246

My own figures were deduced from solidifying point determinations.

As regards the titration figures of Messrs. DE LEEUW and POLAK it must be observed that the end reaction was obtained within one drop of *n*/10 alkali so that there can be only a doubt as to one drop more or less. This represents $\frac{1}{200}$ millimol. or about 0.3 % of the quantity taken for analysis. If we consider further that the above figures are deduced from the tables communicated above, the figures of which present inaccuracies of the same order, the difference between the above percentages may be about 0.6 without exceeding the errors inherent to the process.

From this point of view Mr. POLAK's figures may be pronounced excellent ones. It appears from the table that when the molecular weights found approach more closely to the calculated ones, the percentage of the byproducts is higher. This is easy of explanation. For the nitration product may be considered all the purer when there exists a closer agreement between the calculated molecular weight and that actually found. As, however, the impurities are dissolved on shaking with water, and count as main product in the titration, the figures of this become too high and those of the byproducts consequently too low.

For this reason the following percentages, showing the composition of the nitration products, must be considered as being nearest to the truth.

	I. Nitration of <i>m</i> -chlorobenzoic acid		II. Nitration of <i>m</i> -bromobenzoic acid	
	byprod.	mean prod.	byprod.	main prod.
Temp. 0°.	8	92	13	87
Temp.—30°.	7	93	11	89

The uncertainty of the figures obtained from the solidifying point determinations is a little greater, owing to the circumstance that the mass darkens during the fusion, which causes the solidifying points (which are rather high) to be determined with less sharpness than is usually the case.

August 1908.

Amsterdam, Org. chem. lab. University.