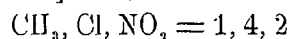


Citation:

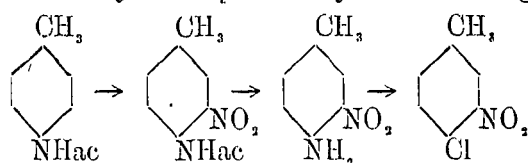
A.F. Holleman, The nitration of p-chlorotoluene., in:
KNAW, Proceedings, 11, 1908-1909, Amsterdam, 1909, pp. 257-260

Chemistry. — “*The nitration of p-chlorotoluene.*” By Prof. A. F. HOLLEMAN.

The *p*-chlorotoluene required for this purpose was prepared by Mr. VAN DEN AREND from pure *p*-toluidine b. p. 160—161° at 754 mm.; m. p. + 7°. Of both nitro-*p*-chlorotoluenes the isomer



was obtained by him from *p*-chlorotoluene by nitration and separation of the mononitrocompounds; it melted at + 38°. He prepared the other isomer $\text{CH}_3, \text{Cl}, \text{NO}_2 = 1, 4, 3$ according to GATTERMANN'S method B. 18,1483 which may be expressed by the following scheme:



The product obtained had a boiling point of 259—260° at 759 mm. and melted at + 7° in a capillary tube. The solidifying point was + 5°8.

For the determination of the relative quantities of both isomers present in the nitration product of *p*-chlorotoluene the solidifying point determination process was again found to be the most suitable. Hence the solidifying point curve of these isomers had to be determined. Mr. VAN DEN AREND obtained the subjoined figures:

% 2-NO ₂ -4-Cl-toluene	Initial solidifying point	End solidifying point
100.0	+ 38°2	—
57.0	+ 9°7	—7°9
44.7	+ 1°4	—8°2
34.8	— 6°3	—
29.8	— 7°2	—
24.1	— 4°1	—8°2
17.5	— 0°5	—
14.1	+ 0°4	—
6.6	+ 4°5	—
0.0 (100% 3-NO ₂ -4-Cl-toluene)	+ 5°8	—

Of these the following figure is the graphic representation.

For the sp. gravities of both isomers and for some of their mixtures, Mr. VAN DEN AREND found the following figures, corrected for upward air pressures and for the expansion of the glass of the pycnometer. The temperature was 80°0.

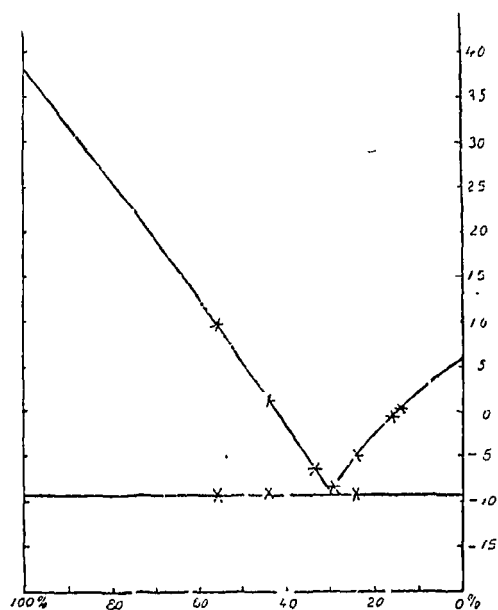


Fig. 1.

Solidifying point line of *p*- and *o*-nitrotoluene.

2-nitro-4-chlorotoluene	calculated
100%	1.2559
57.0	1.2477 1.2446
17.5	1.2364
0.0% (100% 3-nitro-4-chlorotoluene)	1.2296

In the subjoined graphic representation they have been united. The calculated value is the one which the sp. gr. ought to have according to the straight line in the figure, so without contraction. The latter is therefore rather considerable.

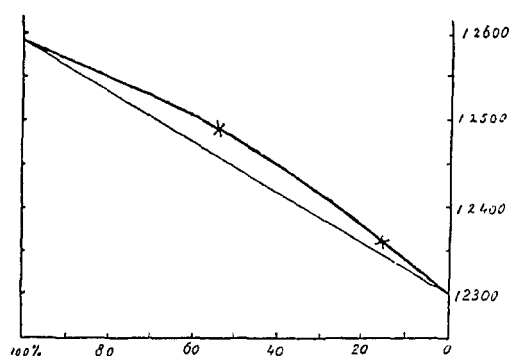


Fig. 2.

Line of the specific gravities for mixtures of the mono-nitro-para-chlorotoluenes.

It was only after some unsuccessful efforts that we succeeded in carrying out the nitration of *p*-chlorotoluene with nitric acid, in that sense that everything was just nitrated, without formation of any dinitro-products. Mr. VAN DEN AREND could ascertain this by determining the specific gravities. As in the case of pure toluene it was again found practical, in order to avoid the formation of higher products of nitration, to add the nitric acid to the *p*-chlorotoluene and not reversedly.

10 grams of *p*-chlorotoluene were cooled to 0°. At that temperature it solidifies to large leaf-like crystals; at the moment of crystallisation setting in, nitric acid (D. 1.48) was added, drop by drop, with thorough shaking. After 1 cc of acid had been added all the crystals had already fused. The liquid turns very dark and consists at first of two layers. After further addition of acid, the temperature being kept at 0° the colour turns pale yellow and the liquid becomes homogeneous. When this point was reached the further addition of acid was stopped and after a few moments the liquid was poured into water. In all, four times the weight of nitric acid was used. The pale yellow oil which collected at the bottom was agitated repeatedly with water until no further acid reaction was noticed, and then dried over sodium sulphate. The following day, the nitration product was distilled twice in vacuo when a slight black residue was left behind. The yield of purified product was 12 grams. It had an initial solidifying point of +10°.2 and an end solidifying point of -8°.0. From the first figure it follows that the nitration product must contain 58% of $\text{CH}_3\text{ClNO}_2 = 1, 4, 3$, whilst the figure for the end point, which coincides with the eutectic point, shows that the mixture contains no other substances besides these two. This was also proved by the sp. gr. which was found to be 1.2481 for an artificial mixture of this composition, whilst the nitration mixture possessed the same sp. gr. Mr. DE LEEUW who also nitrated *p*-chlorotoluene in the manner described, found the initial solidifying point of his product +10°.9, the end point -8°.3. This initial point corresponds with 58.8% 1.2.4.

Mr. VAN DEN AREND also mixed an artificial mixture of both isomers containing 58% 1.2.4 and 42% 1.3.4 with the nitration product in about equal quantities; the mixture so obtained solidified at +10°.3.

It may, therefore, be taken as proved that the nitration product has the above composition. A chlorine determination according to Carius gave 20.3% (calculated 20.7%).

Two nitrations were carried out at +30° in the manner described, using nitric acid (D. 1.45) which both yielded a product the sp. gr. of which was much too high. It appeared that at this

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° , 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].