

*Citation:*

A.F. Holleman, The Nitration of Benzene Fluoride, in:  
KNAW, Proceedings, 6, 1903-1904, Amsterdam, 1904, pp. 659-665

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday March 19, 1904.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 19 Maart 1904, Dl. XII).

CONTENTS.

- A. F. HOLLEMAN: "The nitration of Benzene Fluoride", p. 659.  
JAN RUTTEN: "Description of an apparatus for regulating the pressure when distilling under reduced pressure." (Communicated by Prof. S. HOOGEWERFF), p. 665.  
H. KAMERLINGH ONNES: "Methods and apparatus in the cryogenic laboratory. VI. The methylchloride circulation", p. 668. (With 2 plates).  
H. KAMERLINGH ONNES and H. HAPPEL: "The representation of the continuity of the liquid and gaseous conditions on the one hand and the various solid aggregations on the other by the entropy-volume-energy surface of GIBBS", p. 678. (With 4 plates).  
P. VAN ROMBURGH: "On Ocimene." (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 700.  
P. VAN ROMBURGH: "Additive compounds of s. trinitrobenzene." (Communicated by Prof. C. A. LOBRY DE BRUYN), p. 702.  
E. VERSCHAFFELT: "Determination of the action of poisons on plants." (Communicated by Prof. C. A. LOBRY DE BRUYN and Prof. HUGO DE VRIES), p. 703.  
W. EINTHOVEN: "On some applications of the string-galvanometer", p. 707.  
A. F. HOLLEMAN: "Action of hydrogen peroxyde on diketones 1,2 and on  $\alpha$ -ketonic acids", p. 715  
L. E. J. BROUWER: "On a decomposition of a continuous motion about a fixed point  $O$  of  $S_4$  into two continuous motions about  $O$  of  $S_3$ 's." (Communicated by Prof. D. J. KORTWEG), p. 716  
C. A. LOBRY DE BRUYN and L. K. WOLFF: "Can the presence of the molecules in solutions be proved by application of the optical method of TYNDALL?" p. 735.  
J. J. BLANKSMA: "On the substitution of the core of Benzene." (Communicated by Prof. C. A. LOBRY DE BRUYN and A. F. HOLLEMAN), p. 735.

The following papers were read:

**Chemistry.** — "*The Nitration of Benzene Fluoride.*" By Prof.  
A. F. HOLLEMAN.

(Communicated in the meeting of February 27, 1904).

Dr. BEEKMAN who made some communications in his dissertation as to the above nitration came, although his experiments remained unfinished, to the conclusion that in this case the isomeric mononitrocompounds are formed in quite a different proportion as in the nitration of the other halogen benzenes. As it appeared to me very

44

Proceedings Royal Acad. Amsterdam. Vol. VI.

important to further confirm this statement and as Dr. BEEKMAN could not undertake this himself, I have studied this subject once more and now communicate the results obtained.

The difficulty which presented itself was that we were unable to obtain benzene orthonitrofluoride so that it was impossible to apply the methods which, in the case of the products of nitration of the other halogen benzenes, lead to the knowledge of the proportion in which the isomers are formed. Two observations by Dr. BEEKMAN furnished us, however, with a key to find the said proportion. These were: 1. the very ready transformation of benzene *p*-nitrofluoride with sodium methoxide into the corresponding anisol; 2. the further nitration of the benzene orthonitrofluoride present in the nitrating mixture to benzene dinitrofluoride ( $\text{Fl} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 4$ ) which compound has been obtained by Dr. BEEKMAN in a pure condition.

I convinced myself in the first place of the quantitative course of the transformation of benzene *p*-nitrofluoride with  $\text{NaOCH}_3$ .

1.8347 grams of *p*- $\text{NO}_2 \text{C}_6\text{H}_4$ ,  $\text{Fl} = 13.01$  millimols. were dissolved in a very little pure methyl alcohol, an equivalent quantity of sodium methoxide dissolved in methyl alcohol to the concentration of 0.75 normal was added and the mixture was heated in a reflux apparatus for fully one hour in the boiling waterbath. The liquid still possessed a faint alkaline reaction but became neutral on our adding a trace of dilute acetic acid. On pouring it into water a very beautiful white mass was precipitated which was drained and then air-dried. Without being recrystallised it exhibited a melting point of  $52-53^\circ$ , showing it to be pure *p* nitranisol.

On the other hand in this dilution benzene metanitrofluoride is but very little affected by treatment with sodium methoxide for one hour in the boiling waterbath

1.0842 grams *m*- $\text{NO}_2 \text{C}_6\text{H}_4$ ,  $\text{Fl} = 7.7$  millimols. were mixed with 10 c.c. of  $n_{1.295}$   $\text{NaOCH}_3$  this being the equivalent quantity. After being diluted with water, the liquid was titrated back with 7.50 cc. of *n* acid, theory requiring 7.7 cc. Only 0.2 millimols of the compound had therefore, been decomposed, or 2.6 % of the total amount.

This renders it possible to quantitatively determine the amount of benzene *p*- and *m*-nitrofluoride in a mixture of the two compounds as shown by the following experiments:

*a.* 1.1040 grams = 7.83 millimols. of a mixture of 89 % of the para and 11 % of the meta compound were mixed with 10.1 cc. of  $n_{1.295}$  sodium methoxide and heated in a reflux apparatus for one hour in the boiling waterbath. After being poured into water the liquid was titrated back with 0.8 cc.

of *n* acid corresponding with 0.82 millimols of *meta* if we apply the correction of 2.6% for the *meta* compound attacked. 0.82 millimols = 10.5% of the *meta* compound.

b. 1.1250 grams = 7.98 millimols. of the said mixture were treated in an analogous manner with the equivalent quantity (16.9 cc.) of  $n_{2.12}$  sodium methoxide. The liquid was then titrated back with 0.85 cc. of *n* acid, corresponding, after applying the correction, with 0.87 millimols. of the *meta* compound, or 10.9%. Taking the mean of these two experiments we find 10.7% of the *meta*-compound.

Dr. BEEKMAN had observed that benzene dinitrofluoride ( $\text{Fl}:\text{NO}_2$ :  $\text{NO}_2 = 1:2:4$ ) is converted at 15° in a few minutes into the corresponding anisol by the action of sodium methoxide. This circumstance might be taken advantage of for the quantitative determination of this dinitro compound in the presence of benzene *p*-nitrofluoride if the latter should suffer no change. This was, indeed, the case:

1.0085 grams of the *para* compound were treated at 15° for 5 minutes with 9.53 cc. of  $n_{1.91} = 5$  cc. *n* sodium methoxide. After being poured into water the liquid was titrated back with 5 cc. of *n* acid.

A mixture of the two gave the following result:

1.1680 grams of a mixture containing 10.9% of the dinitro compound were digested at 15° for 5 minutes with 17.6 c.c. of  $n_{2.12}$  NaOCH<sub>3</sub>. The liquid was then titrated back with 7.6 cc. of *n* acid; there was, therefore, present a quantity of dinitro compound of  $\frac{17.6}{2.12} - 7.6 = 0.7$  millimols, or 0.1302 gram corresponding with 11.1% of the dinitro compound.

The above observations rendered it possible to quantitatively determine any benzene di- or metanitrofluoride eventually present in a nitration product of benzene fluoride. In order to determine the benzene orthonitrofluoride contained therein, I converted this into the dinitrocompound by renewed treatment of the nitration product with concentrated nitric acid. Dr. BEEKMAN had found that a further nitration took place (as shown by the increased sp. gr.) when the said product was treated for half an hour at 0° with five times its weight of nitric acid of 1.52 sp. gr., but that even after this treatment, traces of benzene orthonitrofluoride may still be detected by boiling the compound with aqueous sodium hydroxide which yields *o*-nitrophenol. On the other hand Dr. BEEKMAN showed that pure benzene *p*- and *m*-nitrofluoride are quite unaffected by this renewed treatment. In order to get a further and complete nitration of the ortho compound, I prolonged the time of the renewed treatment with nitric acid to one hour after first ascertaining whether benzene

*p*-nitrofluoride is unaffected thereby. This did not seem to be quite the case, so a small correction has to be applied:

*a.* 2.95 grams of pure  $p\text{-NO}_2\text{C}_6\text{H}_4\text{F}$  were treated at  $0^\circ$  with five times the weight of fuming nitric acid of 1.52 sp. gr. The compound rapidly dissolved without elevation of temperature. After one hour the liquid was poured into ice water and the fluorine derivative was instantly precipitated in a solid condition. When the liquid had become clear it was carefully filtered and the mass was repeatedly triturated in ice water until the acid reaction had completely disappeared. It was then treated with 9.65 cc. of  $n_{1.93}$  NaOCH<sub>3</sub> for 5 minutes at  $15^\circ$ . The liquid was then titrated back with 4.77 cc. of *n* acid. This gives  $\frac{9.65}{1.93} - 4.77 = 0.23$  cc. of *n* alkali consumed, corresponding with 0.428 gram of dinitro compound, or 1.4%.

*b.* 1.732 grams of the para compound were treated in the same manner. But after the acid had been removed by washing, the residue was melted to a clear liquid by applying a gentle heat. It was then cooled in ice water and again triturated and washed in ice water until the last traces of acid had disappeared: it was then treated as in *a.* 10.48 cc. of  $n_{1.93}$  NaOCH<sub>3</sub> were used and the liquid was titrated back with 5.3 cc. *n* acid; 0.1 cc. of *n* alkali had therefore been absorbed corresponding with 0.186 gram of dinitro compound or 1.0%. The mean of the two determinations is therefore 1.2%.

Being in possession of these data, I have now subjected the nitration product of benzene fluoride to the same test. Dr. BEEKMAN had previously found that the nitration at  $0^\circ$  with a mixture of 25 cc. of nitric acid of 1.48 sp.gr., 5 cc. acid of 1.51 sp. gr. and 10 grams of benzene fluoride yields a compound consisting solely of mononitro compound (to judge from its percentage of nitrogen; found 9.95 calculated 9.93). I, therefore, nitrated in the same manner and purified the product, which in ice water is semi-solid, by first washing it in ice water, being careful not to lose any oily globules, and then with water at  $20^\circ$ , which caused the whole mass to melt to a homogenous liquid. After all acid reaction had disappeared the bulk of the water was removed by means of a separatory funnel, the clear pale yellow oil was freed from a few drops of adhering water by means of a strip of filterpaper and then finally heated in a testtube at  $90^\circ$ — $100^\circ$  until it no longer became hazy on cooling. We may assume that all the moisture has then been removed, likewise small quantities of any unchanged benzene fluoride. The product so obtained solidified after inoculation at  $18^\circ.7$ ; a second preparation at  $18.6$ .

It does not contain benzene dinitrofluoride:

1.4115 grams were treated for 5 minutes with 9.45 cc. of  $n_{1.93}$  sodium methoxide. The liquid was titrated back with 4.9 cc. *n* acid, or 9.46  $n_{1.93}$  acid.

But on the other hand it contains benzene metanitrofluoride:

a. 5.208 gram of the nitration product = 36.9 millimols. were heated with the equivalent quantity, namely 78.5 c.c., of  $n_{D_{12}}$  sodium methoxide for one hour in the boiling waterbath. After being poured into water, the liquid was titrated back with 1.5 c.c.  $n$  acid; this after correction corresponds with 0.2170 gram of meta compound or 4.2 %.

b. 5.817 gram of the nitration product = 41.3 millimols were treated in the same manner with the equivalent quantity, namely 79.7 cc. of  $n_{D_{13}}$  sodium methoxide. The liquid was titrated back with 1.55 c.c.  $n$  acid; which after correction for the attacked meta compound (2.6 %) corresponds with 0.2243 gram, or 3.9 % meta compound. The mean of the two determinations is, therefore, 4.1 %.

In this determination of the quantity of meta compound it has been assumed (and such is very probably the case) that the benzene orthonitrofluoride present in the nitration product also reacts quantitatively with sodium methoxide.

By renewed treatment of the nitration product with concentrated nitric acid in the manner described, its solidifying point does not perceptibly alter, for it was found to be at  $18^{\circ}.8$ . This had already been noticed by Dr. BEEKMAN. Still, the twice nitrated product now contains benzene dinitrofluoride:

a. 1.0015 gram of twice nitrated product was left in contact for 5 minutes at  $15^{\circ}$  with 8.45 cc. of  $n_{D_{11}}$  sodium methoxide. The liquid was titrated back with 3.9 cc.  $n$  acid. Therefore, alkali absorbed  $\frac{8.45}{1.91} - 3.9 = 0.5$  cc.  $n$  alkali = 0.093 gram dinitro compound, or 9.3 %.

b. 2.264 grams were treated in an analogous manner with 10.15 cc. of  $n_{D_{11}}$  sodium methoxide. The liquid was titrated back with 4.25 cc.  $n$  acid. Alkali consumed, therefore  $\frac{10.15}{1.91} - 4.25 = 1.06$  cc. corresponding with 0.197 gram, or 8.7 % dinitro compound. The mean of the two determinations is, therefore, 9.0 %.

Now we have seen that by treating pure benzene p-nitrofluoride with strong nitric acid for one hour 1.2% undergo further nitration. In the twice nitrated mixture there is present 9% of dinitro- and 4% of meta compound <sup>1)</sup>, therefore 87% of para; 1.2% of this represents 1% of the whole. This quantity of 1% must, therefore, be deducted from the amount of benzene dinitrofluoride found, in order to obtain the quantity which owes its existence solely to the

<sup>1)</sup> 9.0% dinitro = 6.4% mononitro. By subsequent nitration, 100 parts of the once-nitrated product increase to  $100 + (9.0 - 6.4)$  or 102.6 parts which contain 4.1 parts of meta, or 4%.

subsequent nitration of the benzene o-nitrofluoride. This, therefore, amounts to 8%, corresponding with 6.1% of ortho compound. According to the above the composition of the nitration product is therefore :

6.1%	benzene ortho nitro-fluoride	} Being formed by nitration of benzene fluoride at 0° with the concentration of the acid stated on p. 662.
4.1%	„ meta „	
89.8%	„ para „	

The composition of the twice nitrated product was found to be 9% of benzene dinitrofluoride, 4% of meta- and 87% of para compound. This was easily controlled by making an artificial mixture having this composition as all the three components were at disposal. Its properties must then be identical with that of the twice nitrated product. And indeed, the solidifying point of such a mixture was found to be 18°.7 and 18°.9 whilst that of the said product was at 18°.8. According to BEEKMAN's data <sup>1)</sup>, the sp. gr. of the artificial mixture should amount to 1.2773, whereas 1.2791 was found for the twice nitrated product. This higher figure is, probably, to be attributed to the fact that the corrections to be applied are somewhat uncertain so that the results could only be accurate to within about 1%. If this should cause a little excess of dinitro and a little deficiency of meta compound, the sp. gr. will be at once seriously affected, whilst the solidifying point does not perceptibly alter. In fact, an excess of 0.8% of dinitro compound is sufficient to explain the difference in the sp. gr.

I have also endeavoured to nitrate benzene fluoride at -30°, using the same acid mixture employed in the nitration at 0°. On adding the fluoride drop by drop to the acid cooled to that temperature it dissolves with a dark brown colour causing but little rise in temperature, just as had been observed in the nitration of benzene bromide. After all the benzene fluoride had been added, the colour gradually began to fade and when the nitration vessel was removed from the refrigerating mixture and its contents reached a temperature of about -20°, the liquid soon became pale yellow and the temperature rose to about +10°. It, therefore, appears that the velocity of nitration at -30° is already considerably retarded, as the introduction of each drop of benzene fluoride at 0° is accompanied by a very perceptible caloric effect. The solidifying point of the product which was collected in the way described, was situated at 19°.1, from which it may be concluded that it differs but little from the product obtained by nitration 0°. This can only contain about 1% less of by-products.

<sup>1)</sup> Sp. gr. meta 1.2532; para 1.2583; dinitro 1.4718, all at 84°.48.

Let us now see what the quantitative determinations of the nitration products of the halogen benzenes have taught us:

	$C_6H_5Fl.$	$C_6H_5Cl.$	$C_6H_5Br.$	$C_6H_5J$	
ortho . . . .	6.1	29.8	37.6	34.2	} nitration temp. 0°.
meta. . . . .	4.1	0.3 (?)	0.3 (?)	—	
para. . . . .	89.8	69.9	62.1	65.8	
ortho . . . .	—	26.6	34.4	35.3	} nitration temp. -30°.
meta. . . . .	—	0.3 (?)	0.3 (?)	—	
para. . . . .	—	73.1	65.3	64.7	

From this nitration of benzene fluoride it is also shown in the plainest manner that the influence of the fluorine atom on the position of the nitro group is quite different from that of other halogens which in this respect behave very similarly.

*Groningen, Dec. 1903.*

*Lab. Univers.*

**Chemistry.** — “*Description of an apparatus for regulating the pressure when distilling under reduced pressure.*” By JAN RUTTEN. (Communicated by Prof. S. HOOGWERFF).

(Communicated in the meeting of February 27, 1904).

When distilling under reduced pressure it is always of importance to keep this constant during the distillation: moreover, the pressure during the operation must frequently be a definite one. This is, for instance, the case in the testing of mineral oils, where it is generally required that a definite quantity shall distill over at a definite pressure, which is in general considerably less than that of the atmosphere, and at a definite temperature.

As it is not possible to keep the pressure sufficiently constant by the admission of air, the quantity of which is regulated by a screw-