

Citation:

A.F. Holleman, The nitration of disubstituted benzenes, in:
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If l is a chord of R^9 then \mathcal{A} degenerates into two surfaces T^{94} and a surface of degree 100.

If l is a line cutting R^9 once then \mathcal{A} consists of two parts, which will be successively of degree 94 and 194.

4. The numbers $\sigma\rho = 510$ and $\sigma\mu = 165$ furnish well known results.¹⁾ The first tells us that the skew surface ρ^{42} of the trisecants of R^9 possesses a double curve of degree 255; for each plane through a double point of a pair of lines is to be regarded two times as tangent plane. The second number furnishes the property that the threefold tangent planes of the surfaces S^3 of a pencil envelop a surface of class 55.

The surface (P) contains thus 165 right lines lying three by three in 55 planes.

The numbers $\nu\rho$ and $\mu\rho$ furnish with reference to the plane at infinity the following properties:

The parabolae of the congruence form a surface of degree 354, their planes envelop a surface of class 138.

Each S^3 contains 108 parabolae.²⁾ As a definite S^3 can cut the parabolae on the other S^3 only in points of the basecurve R^9 the locus of the parabolae passes $(3 \times 354 - 2 \times 108) : 9 = 94$ times through R^9 .

So through each point of R^9 pass 94 parabolae.

Chemistry. — *“The nitration of disubstituted benzenes.”* By Prof.

A. F. HOLLEMAN.

(Communicated in the meeting of September 24, 1904).

If we introduce into a benzene derivative C_6H_5X a second atom or group this takes up in respect to X a position either chiefly meta or para-ortho depending chiefly on the nature of X . The cause of this is as yet obscure. The efforts for elucidating this phenomenon are totally inadequate, first of all because they are too vague, secondly because they do not take into account the relative quantities which are formed from the isomers; in fact they could not do so, as these were still unknown at the time that these “explanations” were given. A better insight into this problem can only be rendered possible by the quantitative study of the substitution process, which has

¹⁾ KLUYVER, page 152.

²⁾ J. DE VRIES, *La configuration formée par les vingt-sept droites d'une surface cubique*, Arch. Néerl., sér. 2, t. VI, p. 148.

already been made in a number of cases of nitration of the substances C_6H_5X .

For the present we must content ourselves with accepting the results of those quantitative studies as facts. Doing this, we may put the following question: Given a benzene derivative C_6H_4XY , in which a third group Z is introduced. If now we know the relative quantities of the isomers of both C_6H_4XZ and C_6H_4YZ which are formed by the introduction of Z into C_6H_5X and into C_6H_5Y ; can we then deduce from this the structure and relative quantities of the isomers C_6H_3XYZ which are formed by the introduction of Z into C_6H_4XY ?

Suppose (by way of an example) that we have determined how much para- and ortho-compound is formed in the nitration of chlorobenzene and how much meta- and ortho-benzoic acid in the nitration of benzoic acid; can we then determine beforehand which and how much of the possible nitrochlorobenzoic acids will be formed in the nitration of chlorobenzoic acid?

Qualitatively this problem has been studied rather fully, but as a rule not very systematically. In a great many cases it has been determined which of the possible isomers C_6H_3XYZ are formed by the introduction of Z into C_6H_4XY and one has tried to draw conclusions therefrom which render it possible to predict what may be expected in unknown cases. BEILSTEIN has summarised these as follows: "In the introduction of a group Z into a substance C_6H_4XY both X and Y exert an influence but that of one of these groups is predominant and directs Z ."

Undoubtedly, this rule is correct in a great many cases, but not in a good many others. For instance it cannot be applied to the nitration of m-nitroanisole, which I have investigated. In any case it shows that the groups X and Y do not exert their directing influence independently of each other but that this is modified by their simultaneous presence. This has been fully confirmed by a quantitative investigation in the case of a number of nitrations of the compounds C_6H_4XY .

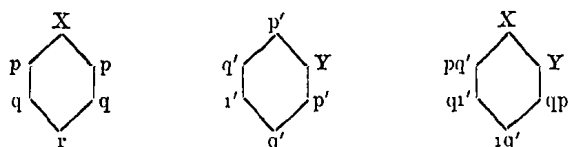
If the groups X and Y exerted a directing influence on a third substituent independently of each other we ought to have the following: If we call the proportion in which the three isomers are formed when Z is introduced into C_6H_5X

$$P_{ortho} : Q_{meta} : R_{para}$$

and that of the three isomers when Z is introduced into C_6H_5Y

$$P'_{ortho} : Q'_{meta} : R'_{para}$$

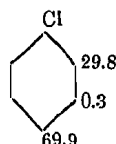
the quantity of the isomers, when introducing Z into C_6H_4XY , would be expressed by products as pq' etc. as shown by the subjoined scheme:



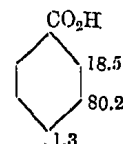
In this it has been supposed that on introducing a second group into a monosubstituted benzene derivative all the three possible isomers are formed, which in practice will most likely be the case even if the quantity of one of these should be so small as to be generally overlooked. In fact, in a number of cases where at first only two substituents had been found, such as in the nitration of nitrobenzene, a careful investigation also revealed the presence of a third one.

The quantitative investigation as to the relative quantities of the isomers which are formed in the nitration of substances C_6H_4XY now showed that those quantities generally differ very considerably from the products pq' etc. so that a serious diversion of the directing influence on the third substituent must be admitted. This diversion was found to depend not only on the nature of the substituents but also on their place in the molecule as proved by the following example.

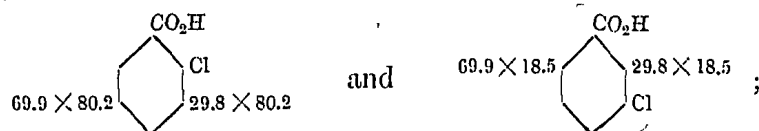
In the nitration of chlorobenzene at 0° para-, ortho- and meta-nitrochlorobenzene are formed in the following quantities:



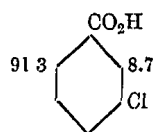
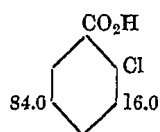
In that of benzoic acid ~
the nitrobenzoic acids in
the following proportion :



If CO_2H and Cl did not modify each other's directing influence, nitroderivatives obtained in the nitration of ortho- and metachlorobenzoic acid would be formed in the quantities indicated in the subjoined schema :



of the other possible isomers only very insignificant quantities. These were in fact so trifling that they were not found. Of the two isomers to be expected in both cases, the relative quantity ought to be just as large as that which is formed in the nitration of chlorobenzene itself. Instead of this was found:



In the subjoined table a number of such observations have been collected. By "diversion" is meant the quotient of the quantity of the byproduct actually found and that of the quantity calculated.

Nitration of	Amount of byproduct on 100 parts of main prod.		Diversion of the directing influence of the halogen of carboxyl.			
	at -30°	at 0°	at -30°	at 0°	at -30°	at 0°
C ₆ H ₅ Cl	36.4	42.0				
C ₆ H ₅ Br	52.7	60.5				
C ₆ H ₅ CO ₂ H	16.9	23.1				
			at -30°	at 0°	at -30°	at 0°
o-C ₆ H ₄ Cl.CO ₂ H	16.3	19.1	0.448	0.455	—	—
o-C ₆ H ₄ Br.CO ₂ H	20.6	24.4	0.391	0.403	—	—
m-C ₆ H ₄ Cl.CO ₂ H	9.1	9.5	0.250	0.226	0.539	0.411
m-C ₆ H ₄ Br.CO ₂ H	13.4(?)	12.9	0.254(?)	0.213	—	0.601
o-C ₆ H ₄ Cl ₂	5.5	7.8	0.151	0.186	—	—
m-C ₆ H ₄ Cl ₂	2.7	4.1	0.074	0.098	—	—

In the nitration of o-halogenbenzoic acid and of o-dichlorobenzene the NO₂-group in the byproducts places itself *adjacent* to the halogen; in that of the m-dichlorobenzene *between* the carboxyl and the halogen. On comparing the diversion figures of the directing influence of the halogen in these acids and dihalogen-compounds, those of the meta-compounds amount to about half of the ortho-compounds. This is one of the many cases which show that the introduction of a substituent between two others meets with a particularly great resistance.

Groningen, Lab. Univers. Aug. 1904.