

Studies on Catalytic Action, XX.

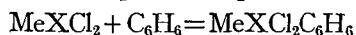
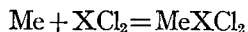
Catalytic Chlorination I.

By

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It was well known that when chlorine gas comes into contact with benzene in presence of some catalyst, monochlorobenzene was formed,¹ and iron powder,² aluminium-mercury couple³ and aluminium chloride have proved most suitable for this purpose. The mechanism for the catalytic action, as we explained in the Friedel-Crafts reaction, is supposed to take place in stages: first, an unstable compound from the catalyst and chlorine being formed, which then reacts with benzene to form an intermediate additional compound of the type $\text{MeCl}_x\text{C}_6\text{H}_6$, and the latter is then broken down with the formation of chlorobenzene and hydrochloric acid.



Although Copper⁵ probably with iron⁶ and zinc may be used as a

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- 1 P. Sabatier: *La catalyse en chimie organique* (1920) p. 102; Holleman & van der Linden: *Rec. trav. chim.*, **30**, 305 (1911); A. E. Holleman: *Die directe Einführung von substituenten in der Benzolkern* (1910).
 - 2 A. Sator: *J. Chem. Soc.*, **83**, 729 (1903).
 - 3 Cohen & Dakin: *Ibid.*, **79**, 1196 (1910).
 - 4 Mouneyrat & Pouret: *C. R.* **127**, 1026 (1898).
 - 5 Zincke: *Lieb. Ann.*, **159**, 367 (1871).
 - 6 Nencki: *Ber. D. Chem. Ges.*, **30**, 1766 (1897); **32**, 2414 (1899).

catalyst, in place of aluminium, in the Friedel-Crafts reaction, the catalyst seems to behave in a somewhat different manner from other catalysts for a mixture of chlorine and benzene, since this metal, as we observed its behavior in the Deacon process, by the action of chlorine, was transformed into cupric chloride which decomposed into cuprous chloride and chlorine. When pure and dry benzene was passed with dry chlorine gas on reduced copper obtained by the reduction of the copper oxide formed by the ignition of copper nitrate with a slow current of hydrogen at 200° C, the catalyst was noticed to change into a mixture of cuprous and cupric chlorides, in the progress of reaction, with evolution of hydrochloric acid, which indicates that some reaction had happened to the benzene. The reaction product composed of a yellow liquid and solid substances, and the latter separated from the former by filtration, was confirmed to be composed of benzene-hexachloride $C_6H_6Cl_6$, giving 73.87% of chlorine-content which agrees well with the theoretical value 73.19%.

Benzene being a substance containing three double bonds in its molecule, according to Kékulé's formula, should take up six atoms of chlorine, bromine or hydrogen under certain conditions, and as a matter of fact, benzene was converted by catalytic hydrogenation of reduced copper into hexahydrobenzene.¹ However, benzene hexachloride was usually made by the action of chlorine upon benzene in sunlight or, better, by passing chlorine on benzene suspended in a one per cent sodium hydroxide solution.

In our experiment, 30 grm. of benzene by the action of chlorine at ordinary temperature, yielded 7 grm. of crude benzene hexachloride. Benzene hexachloride, thus obtained, was noticed to be a mixture of α and β isomers, and α or so called trans-modification which was separated from β or the cis-modification according to F. E. Mathews's method² by steam distillation, due to its volatile nature.

α -Benzene Hexachloride (Trans-form)³.

When it was recrystallized from the absolute alcohol solution, melted at 157°, and was decomposed by heating into hydrochloric acid and 1 : 2 : 4-tri-chlorobenzene. On analysis, it gave the following results: Cl=

1 Pease & R. B. Purdum: J. Am. Chem. Soc., **47**, 1435 (1925).

2 J. Chem., Soc., **59**, 165 (1891).

3 Scholl & Norr: Ber. D. Chem. Ges., **33**, 727 (1906).

73.64, theory requires Cl=73.19 for $C_6H_6Cl_6$.

β -Benzene Hexachloride (Cis-form).¹

The non-volatile part which remained in a flask was composed of β -isomer which is soluble in benzene and with difficulty soluble in alcohol, and melts at 297° . It gave, on analysis, Cl=73.07 theory requires 73.19 for $C_6H_6Cl_6$.

The liquid reaction product separated from benzene hexachlorides, was subjected to fractional distillation at ordinary pressure, and divided into the following portions:

	B. P.	Yield	Remark
1.	$80^\circ-100^\circ$	13 gm.	
2.	$120^\circ-140^\circ$	6 "	Liquid
3.	$200^\circ-220^\circ$	8 "	Solidified on cooling with ice-cold water.
4.	$240^\circ-250^\circ$	small	Solidified on cooling.

The first fraction was ascertained to be unchanged benzene, and the second was mono chlorobenzene, from their chemical and physical properties.

1 : 2 : 4-Trichlorobenzene.

The third fraction which shows $d_{25}^{25}=1.4634$; $n_D^{25}=1.5524$, was confirmed to consist of 1 : 2 : 4-trichlorobenzene by converting it into 1 : 2 : 4 : 5-trichlor-nitro-benzene of M. p. 57° by nitration with fuming nitric acid.

1 : 2 : 4 : 5-Tetrachlorobenzene.

The fourth fraction which boils at $240^\circ-250^\circ$, was found to consist of crystals which purified from the alcohol solution, show the same melting point $137^\circ.5$ as that of 1 : 2 : 4 : 5-tetrachlorobenzene.

In order to learn the yield of the compounds above-mentioned, several experiments under different conditions were carried out, and the results are shown in the following table:

¹ Scholl & Norr: Loc. cit.

No.	Reaction temp.	Benzene		Reaction product		
		Used	Changed	Solid	Liquid	
					(120°—140°)	(200°)
1.	ord. tmp.	30 gr.	17 gr.	7 gr. (6.3%)	6 gr.	8 gr.
2.	150°	" "	9 "	2 " (1.6")	6 "	6 "
3.	180°	" "	20 "	18 " (16.0")	6 "	8 "
4.	300°	" "	21 "	32 " (28.5")	2 "	9 "
5.	200°	" "	—	66 " (59.0")	—	—

The formation of benzene hexachloride is favorable at high temperatures, and especially as indicated in No. 5 when the catalyst was previously treated with chlorine, whereas copper was transformed into a mixture of cupric and cuprous chlorides,¹ while at low temperatures mono chlorobenzene and poly chlorobenzene are apt to be produced.

Thus, in the chlorination of benzene, in presence of reduced copper, the reaction as we have stated above, will proceed with the formation of an addition compound on the one hand, and on the other substitution products.

Therefore, the function of reduced copper toward a mixture of chlorine and benzene, as a catalyst, is quite different from that of iron and aluminium, the latter catalysts accelerate mostly the substitution which takes place in a minor degree in the presence of the copper catalyst.

In order to study the influence of the entering group on the chlorination, 20 gm. of pure mono chlorobenzene ($d=1.102$; B. p. = 131° — 132°) prepared from the prior experiment, were passed in an interval of 4 hours along with dry chlorine upon the copper which had already been treated with dry chlorine gas and heated at 200° , and 4.5 gm. of a product with B. p. (140° — 180°) were obtained composed of dichlorobenzene.

In another experiment, 30 gm. of mono chlorobenzene were passed on the catalyst at the rate of 1—2 gm. per hour, and the following reaction products were the result.

1. 11 gm. of a colourless solid substance.
2. 33 gm. of an oily liquid.

and the second product was fractionated:

¹ Mellor: A comprehensive treatise of inorganic & theoretical chemistry vol. III, 157 (1923).

	Fraction	Yield
(A)	to 180°	8.5 gm.
(B)	200°—220°	small
(C)	220°—250°	15 gm.
(D)	above 250°	6.5 gm.

β -Monochlorobenzene Hexachloride (Cis-form)

The solid reaction product was washed with cold alcohol and recrystallized from benzene in transparent crystals which melted at 260°. On analysis, Cl=76.45% ; theory requires Cl=76.34% for $C_6H_5Cl \cdot Cl_6$. The analytical results and properties agree with those of β -monochlorobenzene hexachloride described by Otto.¹

Para-Dichlorobenzene.

From the fraction (A), B. p. to 180°, a solid substance (m. p. 53°) was isolated and purified by recrystallization from alcohol. The yield was 3.5 gm. Cl=47.59% ; theory requires Cl=48.25% for $C_6H_4Cl_2$.

1 : 2 : 4-Trichlorobenzene.

The fraction (B), B. p. 200°—220°, was confirmed to be composed of trichlorobenzene, after converting it by nitration with fuming nitric acid, into 1 : 2 : 4 : 5-trichlor-nitrobenzene (M, p. 57°).

1 : 2 : 4 : 5-Tetrachlorobenzene.

The fraction (C), B. p. 220°—250°, which was composed of the major part of the reaction product, was solidified on standing for a while at room temperature, and recrystallized from alcohol. It melted at 137°.5, Cl=65.68% ; theory requires Cl=65.73% for $C_6H_2Cl_4$.

Pentachlorobenzene.

The last fraction (D), B. p. above 250°, was composed mostly of the penta-chlor compound. It was analysed after purification from alcohol,

¹ Lieb. Ann., 141, 101 (1867).

M. p. 83° — 84° , Cl=69.42% ; theory requires Cl=70.85% for $C_6H_4Cl_2$.

As we have already stated, benzene and chlorine come into contact with reduced copper, benzene hexachlorides (cis & trans) are formed together with a small quantity of mono & poly chlorobenzene. The yield of the addition products was increased to about 60% when the reaction temperature was raised to 200° or when the catalyst was previously treated with dry chlorine gas. However, the substitution of the hydrogen atoms of benzene would be promoted by the influence of the chlorine atom which had already replaced the hydrogen atom of the benzene molecule, being tetrachlorobenzene, one of the prominent substitution products.

It is noteworthy that in the addition reaction of benzene, benzene hexachloride was composed mostly of the α -form, while in the case of monochlorobenzene β -form of the hexachloride only was isolated.

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