CCCCXXXV.—*The Thermal Vapour-phase Chlorination of Toluene and Benzene.*

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THIS work is a continuation of that previously described (Mason and Wheeler, this vol., p. 2282) on the action of chlorine on hydrocarbons and chloro-substitution products in the vapour phase.

It was desired, in the case of toluene, to determine to what extent chlorine enters the nucleus at high temperatures in the absence of specific chlorine carriers, and to determine whether, as regards the kinetics of side-chain chlorination, this hydrocarbon can be regarded as a substituted methane. The thermal vapour-phase chlorination of toluene has been previously examined by Ellis (U.S.P. 1,202,040; *B*, 1916, 1212) and Mason (Diss., Oxford, 1929). These authors find that in the absence of specific carriers chlorine enters the side chain. The results of the present work, which has been carried out at higher temperatures and with shorter periods of heating, confirm this finding, and show that the kinetic formulæ of Martin and Fuchs (*Z. Elektrochem.*, 1921, **27**, 150) apply to toluene considered as a substituted methane, if catalysts which promote nuclear chlorination are absent. The general formula giving the percentages of initial substance (*e.g.*, toluene) converted into the *m*th product, in terms only of the total percentage consumed (x), is

$$y_m = \frac{\underline{|n}}{\underline{|m}\,\underline{|n-m}}(100-x)\left[\left(\frac{100}{100-x}\right)^{1/n}-1\right]^m$$

where n is the number of bimolecular stages involved. According to the formula ($n = 3$) the maximum yield of benzyl chloride (calculated as a percentage of the toluene applied) is 44·4%, with a 70·3% consumption of the applied toluene; the maximum for benzal chloride is not reached until the consumption is 96·3%. That the experimental and theoretical values are in good agreement may be seen from Fig. 1.

With regard to benzene, the main object was to investigate, with particular reference to the formation of monochlorobenzene, the extent to which substitution occurs at high temperatures, in the absence of specific chlorine carriers. No previous work has been done on this subject, although Mouneyrat and Pouret (*Compt. rend.*, 1898, **127**, 1025), quoting Berthelot and Jungfleisch, state that, in the dark, chlorine and benzene do not react below 300°. The experiments to be described showed that direct chlorination to chlorobenzenes takes place in the vapour phase above 400°, mono- and di-chlorobenzenes being the chief products. The rate of reaction is not so great as in the case of toluene. The results, when only mono- and di-chlorobenzenes are formed, are in good agreement with Martin and Fuchs's kinetic formulæ for a two-stage reaction. This is shown in Fig. 2. No attempt was made to separate, one from another, the isomeric dichlorobenzenes. They are sufficiently alike in their physical properties to be treated as a single compound in the method of analysis employed.

EXPERIMENTAL.

(1) *The Action of Chlorine on Toluene.*—The apparatus used was similar to that employed in the previous work, except for modifications necessitated by the fact that toluene and its chlorination products are liquid at ordinary temperatures. The chlorine passed into the reaction tube by way of an inverted T-piece, down the vertical limb of which the required amount of toluene was delivered from a burette. The toluene used distilled within about 1°. The fireclay reaction tubes were of 0·5 cm. and 2·3 cm. diameter, with heated lengths of 15 cm. and 30 cm. respectively. The wider tube was used both empty and packed with fireclay.* The exit gases from the reaction tube, after being cooled to condense unchanged toluene and liquid reaction products, were passed through water and 20% sodium hydroxide solution. Practically complete absorption took place, as the original chlorine (from a cylinder) was 98% pure.

In an experiment, after the apparatus had been swept out with nitrogen, the reaction tube was filled with a measured amount of toluene vapour in order to prevent the reaction mixture burning at the inlet, owing to a local excess of chlorine. The toluene and chlorine flows were then adjusted. At the end of an experiment the chlorine was turned off first, and the reaction products swept out with nitrogen. The contents of the washers were analysed for hydrogen chloride and free chlorine. These were also estimated in the liquid products, being extracted by shaking with 10% sodium hydroxide solution.

As the technical object sought was complete utilisation of the chlorine, experiments in which more than 2·5% remained unchanged were not further investigated. If the conversion was satisfactory, the liquid product was washed with water, dried over calcium chloride, and fractionated through a 6-bulb Young column. Fractions were taken at the mid-points between the boiling points of the

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* The following details were omitted from the previous paper (Mason and Wheeler, *loc. cit.*): Table I—0·4 cm. tube, 15 cm. heated length. Table II—1 cm. tube, 15 cm. heated length, packed except in Expt. 3.

possible constituents (toluene, 110°; chlorotoluenes, 159—162°; benzyl chloride, 179°; benzal chloride, 207°), as recommended by Young ("Distillation Principles and Processes," p. 170). The residue above 210° was less than 1% of the total. It was shown, by distilling a typical synthetic mixture of the constituents, that this procedure gave results within the experimental error. The toluene and chlorine accounted for in each experiment amounted to over 97% of the input.

Results with a 0·5 cm. tube.

Molecular ratio, chlorine : toluene, 1 : 2·2.

		% Toluene applied converted into				% Chlorine applied recovered as	
		benzyl chloride.		benzal chloride.			
Temp.	*S.V.*,* min.$^{-1}$.	Obs.	Calc.†	Obs.	Calc.†	Cl$_2$.	HCl.‡
400°	500	—	—	—	—	23·1	—
500	500	30·5	30·0	2·3	4·6	Nil	56·2
600	500	20·1	19·9	1·6	1·7	Nil	64·1
600	1000	27·1	26·7	5·6	3·5	0·9	51·1
700	3000	22·3	24·2	4·6	2·7	0·9	59·1

* *S.V.* = space velocity, *i.e.*, the number of volumes of gas, at the reaction-tube temperature, passing through the heated volume per minute.

† From Martin and Fuchs's kinetic formulæ.

‡ The excess over 50% of the percentage chlorine as hydrogen chloride can be taken as a measure of the pyrolysis.

In these experiments the lower temperature limit for complete chlorination was 500°. At temperatures above 600° pyrolysis of the products occurred even with space velocities high enough to give unchanged chlorine in the exit gas (*i.e.*, up to 3000 min.$^{-1}$). It was found impossible to work in the temperature range 400—600° with mixtures containing more than 1 vol. of chlorine to 2 vols. of toluene vapour.

Results with a 2·3-cm. tube.

			% Toluene applied converted into				
			benzyl chloride.		benzal chloride.		
Mol. ratio, Cl$_2$: C$_7$H$_8$.	Temp.	*S.V.* (actual), min.$^{-1}$.	Obs.	Calc.	Obs.	Calc.	Unchanged chlorine, % of input.
1 : 1·2	310°	2·7	38·9	39·3	10·8	10·3	0·1
1 : 1·2	315	2·7	37·2	39·5	11·2	10·5	Nil
1 : 1·2	250	2·7*	32·5	38·0	10·4	9·1	0·6†
1 : 1·2	315	28·3*	30·4	31·9	6·9	5·4	Nil†
1·3 : 1	300	6·9*	43·5	44·4	26·3	21·8	0·7†

* Packed tube. Free space/total volume packed = 0·53. Fireclay packing passed through a 10-mm. and was retained by a 3-mm. sieve.

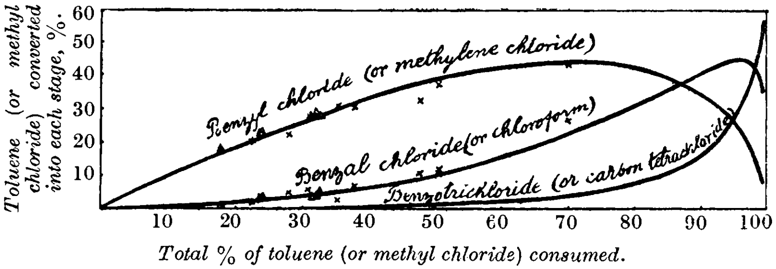
† Much pyrolysis in these experiments.

In order to determine the speed of the vapour-phase reaction at low temperatures, a tube 2·3 cm. in diameter was used.

With a space velocity of 2·7 min.$^{-1}$, complete reaction was not obtained below 310°, but at this temperature a mixture as rich as 1 vol. of chlorine to 1·2 vols. of toluene vapour could be used without inflammation. Increase in the proportion of chlorine increased the amount of toluene consumed, and produced a greater formation of benzal chloride. Little pyrolysis occurred in these experiments.

When the reaction tube was packed with fireclay, it was possible to obtain practically complete reaction at a temperature of 250° using a gas mixture containing 1 vol. of chlorine to 1·2 vols. of toluene vapour. Also, an excess of chlorine, 1·3 vols. to 1 vol., could be used at a temperature of 300°, the proportional formation of benzal chloride being then greatly increased. The presence of packing enhances the tendency to pyrolysis.

FIG. 1.



Continuous curves = theoretical curves for three-stage reaction.
Points marked × = experimental values, chlorination of toluene.
Points marked △ = experimental values, chlorination of methyl chloride.

In the graphical representation of the foregoing results (Fig. 1), it will be seen that only two points differ appreciably from the theoretical curves. This may be explained in one case (benzyl chloride curve) by "much pyrolysis," and in the other (benzal chloride curve) by the possible inclusion of benzotrichloride. The results of a three-stage reaction previously studied, *viz.*, the chlorination of methyl chloride (Mason and Wheeler, *loc. cit.*, Table VI), are also given in Fig. 1.

That in the foregoing experiments most of the chlorine entered the side chain and not the nucleus was shown by the distillation curves of the products, and by the fact that the crude benzoic acid, obtained on oxidation of the products by potassium permanganate, always contained less than 0·3% of chlorine. Experiments with silica reaction tubes free from iron gave the same results.

Effect of catalysts.

Tube diameter, 0·5 cm. Temperature, 500°.
S.V., 500 min.$^{-1}$. Mol. ratio, $Cl_2 : C_7H_8$ = 1 : 2·2.

Catalyst, and wt. per g. of C_7H_8.	% Toluene applied converted into benzyl chloride.	benzal chloride.	chlorotoluenes.
None	30·5	2·3	Nil
I_2, 0·01 g.	12·0	4·0	16·9
NH_3, 0·01 g.	18·9	6·1	9·5
$CHCl_3$, 0·01 g.	28·4	4·8	Nil
$FeCl_3$, see note below	6·7	8·9	14·5
S, see note below	22·1	3·9	3·9
H_2O, see note below	29·0	4·4	Nil

Note.—The first three catalysts were introduced by adding 1% by weight to the toluene. For the last three, the toluene was shaken with the catalyst, and separated. The amounts added by this means were not estimated, and the results in these cases are in this respect qualitative. The substances are all volatile at 500°.

Iodine, ammonia to a less extent, ferric chloride, and sulphur promote chlorination in the nucleus; chloroform and water tend only to increase the proportion of benzal chloride.

(2) *The Action of Chlorine on Benzene.*—The experimental methods were similar to those described in the previous section. The benzene used distilled within about 1°. The silica reaction tubes were heated over a length of 30 cm. For analytical purposes, the volume and density of the liquid product were noted, and an aliquot portion was treated with 3 volumes of 10% sodium hydroxide solution to extract hydrogen chloride and unchanged chlorine. The remainder of the liquid product was neutralised with solid sodium carbonate (the carbon dioxide evolved removes unreacted chlorine), filtered, and distilled through a 6-bulb Young column. Cuts were made at 130° (2° below the b. p. of monochlorobenzene) and 170° (2° below the b. p. of *p*-dichlorobenzene). Each fraction consisted of two components (benzene and monochlorobenzene; mono- and dichlorobenzene; residue, di- and tri-chlorobenzene, where present), and the amount of each constituent was calculated from tables relating composition to density.*

This method of analysis, essentially the same as that of Bourion (*Compt. rend.*, 1920, **170**, 933, 990) and Bourion and Courtois (*ibid.*, p. 1115), was checked on synthetic mixtures. It is suitable for the determination of the monochlorobenzene produced, but owing to the small quantity formed, it is only in the third and fifth tables that the variations in the amount of dichlorobenzene are considered to be significant. The chlorine and benzene accounted for in each experiment amounted to about 95% of the input.

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* The method of analysis and the tables used were supplied by I.C.I. (General Chemicals), Ltd., to whom our best thanks are due.

The results are presented in a series of tables showing the effect of systematic alteration, one at a time, of the variables concerned.

Effect of varying space velocity.

Temperature, 450°. Mol. ratio, $Cl_2 : C_6H_6 = 1 : 2{\cdot}2$.

Tube diam., cm.	*S.V.*, min.$^{-1}$.	% Benzene applied converted into			Unchanged chlorine, % of input.
		C_6H_5Cl.	$C_6H_4Cl_2$.	$C_6H_3Cl_3$.	
0·5	50	32·1	2·7	Nil	Nil*
0·5	100	28·2	4·3	Nil	6·2
0·5	250	22·5	2·2	3·1	20·8
1·0	20	34·6	3·6	Nil	Nil*
1·0	50	34·3	3·7	Nil	0·3
1·0	100	23·7	4·6	Nil	20·6
1·0	160	9·2	2·6	1·9	50·9
2·0	5	34·6	3·7	Nil	Nil*
2·0	10	34·5	3·2	Nil	Nil
2·0	15	35·9	2·7	Nil	Nil
2·0	25	34·0	4·2	Nil	1·1
2·0	50	30·2	3·1	Nil	13·5
2·0	65	16·8	3·5	1·5	28·9

* Carbon deposited.

The results show that with each tube, above a certain limiting space velocity, the percentage of unreacted chlorine increases rapidly. With too long a period of heating, carbon is deposited. Where the amount of unreacted chlorine is high, trichlorobenzene is present; this may be formed from benzene–chlorine addition compounds produced by the reaction of benzene and free chlorine in the condensate from an experiment.

Effect of varying temperature.

Mol. ratio, $Cl_2 : C_6H_6 = 1 : 2{\cdot}2$.
Tube diameter, 1·0 cm.; *S.V.*, 50 min.$^{-1}$.

Temp.	% Benzene applied converted into			Unreacted chlorine, % of input.
	C_6H_5Cl.	$C_6H_4Cl_2$.	$C_6H_3Cl_3$.	
600°	32·5	2·1	Nil	Nil*
500	35·0	3·2	Nil	Nil*
475	35·6	2·6	Nil	Nil
450	34·3	3·7	Nil	0·3
440	33·1	3·6	Nil	0·3
425	25·9	2·5	1·9	11·7
400	15·5	3·8	2·3	31·3
	Tube diameter, 2·0 cm.; *S.V.*, 10 min.$^{-1}$.			
500	31·3	2·7	Nil	Nil*
475	32·6	3·5	Nil	Nil*
450	34·5	3·2	Nil	Nil
425	32·9	3·9	Nil	0·1
400	32·5	3·9	Nil	1·0
375	24·1	2·1	1·0	20·1

* Carbon deposited.

It is evident that for a given space velocity there is a critical temperature below which the amount of chlorine passing through unreacted increases rapidly. Above a certain temperature, pyrolysis sets in and carbon is deposited.

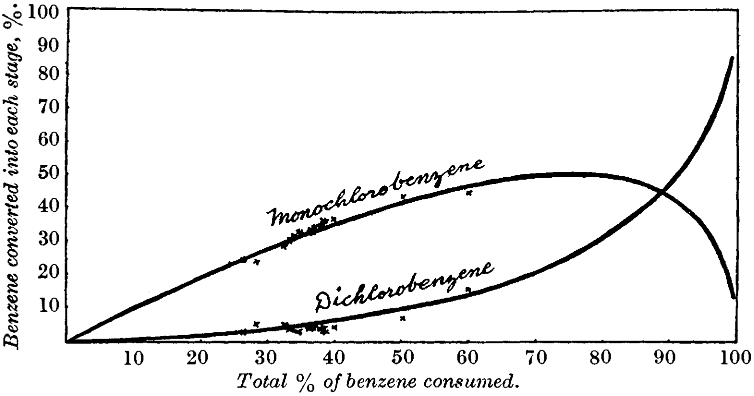
Effect of varying molecular ratio of reactants.

Tube diameter, 1·0 cm. Temp., 450°. *S.V.*, 50 min.$^{-1}$.

Mol. ratio $Cl_2 : C_6H_6$.	% Benzene applied converted into C_6H_5Cl.	% Benzene applied converted into $C_6H_4Cl_2$.	Unreacted chlorine, % of input.	Ratio, $C_6H_5Cl/C_6H_4Cl_2$.
1 : 1·1	44·7	15·2	Nil	2·9
1 : 1·6	43·3	6·8	Nil	6·4
1 : 2·2	34·3	3·7	0·3	9·3
1 : 3·4	24·0	2·2	0·5	10·9

In these experiments trichlorobenzene was not formed.

FIG. 2.



Continuous curves = theoretical curves for two-stage reaction.
Points marked × = experimental values.

The increased production of dichlorobenzene without formation of trichlorobenzene is interesting. When the molecular proportion of benzene to chlorine falls below 1 : 1, inflammation occurs at the entrance to the reaction tube, but can be stopped by momentarily increasing the flow of benzene.

Effect of varying surface–volume ratio.

Tube diameter, 2·0 cm. Mol. ratio, $Cl_2 : C_6H_6$ = 1 : 2·2.

Temp.	*S.V.*, min.$^{-1}$.	% Benzene applied converted into C_6H_5Cl.	% Benzene applied converted into $C_6H_4Cl_2$.	% Benzene applied converted into $C_6H_3Cl_3$.	Unreacted chlorine, % of input.
450°	50	30·2	3·1	Nil	13·5
450	(50)* 94·5	36·3	3·5	Nil	0·3
375	10	24·1	2·1	1·0	20·1
375	(5·3)* 10	27·8	2·0	2·6	9·9

* Packed tube. Free space/total volume packed = 0·53. Silica packing used passed through a 10-mm. and was retained by a 3-mm. sieve. Figures in parentheses give space velocity uncorrected for the volume of the packing.

Packing the reaction tube with broken silica increases the speed of the reaction but does not induce complete reaction at 375° with a space velocity of 10 min.$^{-1}$.

In Fig. 2 the results of those experiments (the preceding four tables) in which no trichlorobenzene was formed are compared graphically with the theoretical curves for a two-stage process. It will be seen that good agreement is obtained.

Effect of catalysts.

Tube diameter, 2·0 cm. Temperature, 450°.
S.V., 50 min.$^{-1}$. Mol. ratio, $Cl_2 : C_6H_6 = 1 : 2{\cdot}2$.

Catalyst, and wt. per g. of C_6H_6.	% Benzene applied converted into			Unreacted chlorine, % of input.
	C_6H_5Cl.	$C_6H_4Cl_2$.	$C_6H_3Cl_3$.	
None	30·2	3·1	Nil	13·5
Iodine, 0·005 g.	32·2	4·4	Nil	2·5
Aluminium chloride, see note below	33·6	4·3	Nil	4·8
Ferric chloride, see note below	28·4	6·3	0·5	0·6

Note.—Iodine was introduced by adding 0·5% to the benzene. The amounts of aluminium chloride and ferric chloride were not estimated, and these results are therefore in this respect qualitative. All the catalysts used are volatile at 450°.

It is clear that the usual liquid-phase catalysts promote chlorination in the vapour phase. With ferric chloride the proportional formation of dichlorobenzene is increased, and a little trichlorobenzene is formed.

Summary.

Chlorine reacts smoothly and rapidly with excess of toluene at temperatures above 250° to give side-chain chlorination products (chiefly benzyl and benzal chlorides). The results obtained are satisfactorily expressed by the kinetic formulæ of Martin and Fuchs for a three-stage reaction. In the presence of a carrier, substitution in the nucleus also occurs.

Chlorine reacts similarly with excess of benzene, at temperatures above 400°, to yield mono- and di-chlorobenzenes, with little or no trichlorobenzene. The rate of reaction is increased by iodine. When only mono- and di-chlorobenzenes are formed, the results are in accordance with Martin and Fuchs's kinetic formulæ for a two-stage reaction.

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