CLII.—*The Chlorination of Toluene.*

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A preliminary note on the above subject was published in 1905 (Trans., **87**, 1034), and in this an account was given of the action of chlorine obtained by the electrolysis of aqueous hydrochloric acid in contact with boiling toluene. The results pointed to a marked difference in the products so obtained from those which are produced by the action of ordinary chlorine under similar conditions.

During the course of further experiments it has been found that diffused daylight acts so rapidly in producing side-chain substitution that comparable results are only possible when light is rigidly excluded. On this account the comparative experiments described in this paper were carried out in the dark. In the second place, a much more rapid and accurate process for estimating the amount of the side-chain and nuclear substitution products was used in place of the former analytical method.

While these experiments were in progress several papers dealing with the closely related question of the bromination of toluene have appeared, and a review of the subject of the chlorination and bromination of benzene and toluene has been published by Bancroft in the third of a series of articles on "The Electrochemistry of Light" (*J. Physical Chem.*, 1908, **12**, 420).

When chlorine acts on toluene, side-chain substitution takes place (1) in sunlight at 0° and higher temperatures (Schramm, *Ber.*, 1885, **18**, 606); (2) in the dark at the boiling point of toluene (Cannizzaro, *Compt. rend.*, 1855, **41**, 517). According to Häussermann and Beck (*Ber.*, 1892, **25**, 2445), side-chain substitution is greatly facilitated in the case of nitrotoluene in presence of sulphur. Sulphur thus appears to behave differently from the usual carriers, such as ferric chloride, molybdenum pentachloride, antimony pentachloride, iodine chloride, pyridine, and the aluminium-mercury couple, for these bring about nuclear substitution.

In contrast with the qualitative nature of the observations relating to the process of chlorination, quantitative measurements showing the influence of various factors on the side-chain and nuclear substitution have been obtained in connexion with the bromination of toluene. The experiments of Holleman, Polak, van der Laan, and Euwes (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 512; *Rec. trav. chim.*, 1908, **27**, 435), and those of Bruner and Dluska (*Bull. Acad. Sci. Cracow*, 1907, 693) have shown that the relative proportion of bromine which enters the side-chain is not only increased by light, but in the dark it is increased by rise of temperature and by dilution of the reacting bromine. The methods adopted in these two series of experiments were not the same, for whereas Holleman and his collaborators used open vessels and only analysed the product obtained when the bromine had completely disappeared, Bruner and Dluska employed sealed tubes and analysed the products at different stages of the reaction.

The influence of the nature of the medium on the distribution of the bromine between the side-chain and the nucleus was also examined by these authors. When the toluene is considerably diluted by admixture with carbon tetrachloride, this distribution is the same as in the case of pure toluene, but dilution to the same extent with nitrobenzene has the effect of decreasing the proportion of the bromine which enters the toluene side-chain. This influence of the medium has been further studied by Bruner and Vorbrodt (*Bull. Acad. Sci. Cracow*, 1909, 221), who investigated the effect of carbon disulphide, carbon tetrachloride, benzene, chloroform, acetic acid, benzonitrile, and nitrobenzene on the bromination of toluene, ethylbenzene, *iso*-propylbenzene, and *o*-, *m*-, and *p*-xylene. They find that the influence of the solvent is not only observable in the dark, but shows itself in the process of photobromination. The effect of nitrobenzene, and to a less extent of acetic acid and benzonitrile, is greatly to diminish the proportion of side-chain substitution.

With regard to the bromination of toluene in the presence of carriers, Bruner and Holleman (*loc. cit.*) and Jackson and Field (*Amer. Chem. J.*, 1881, **2**, 10) have found that side-chain substitution increases with decreasing concentration of the carrier and also with rise of temperature.

In explanation of these various observations, two essentially different views have been put forward. According to Bruner, side-chain substitution is due to molecular bromine, whereas nuclear substitution is effected by bromine atoms or ions, which result from the dissociation of bromine molecules in accordance with the equation:

$$Br_2 \rightleftharpoons Br + Br.$$

The velocity measurements of Bruner and Dluska are cited as evidence in favour of this hypothesis. These determinations indicate that both the side-chain and nuclear substitution processes take place in accordance with the requirements of the equation for a unimolecular change if the concentration of the bromine is small. For higher bromine concentrations, the values obtained for the constant characteristic of a unimolecular change decrease as the reaction proceeds. This is attributed to the withdrawal of active bromine from the solution by the formation of a hydrogen perbromide (HBr_3). Since the dissociation of this perbromide increases as the concentration of the solution diminishes, its influence on the rate of progress of the bromination is inappreciable in the case of dilute bromine solutions.

According to this hypothesis, the action of carriers, such as iodine, consists in forming compounds with bromine which undergo dissociation with the production of bromine atoms or ions in much greater concentration than that which is obtained in the case of a pure solution of bromine. Hydrogen perbromide is supposed to be a dissociating compound of this character, and the increase in the proportion of nuclear substitution which is found when the toluene is mixed with nitrobenzene, benzonitrile, acetic acid, and certain other liquids, is attributed to the relatively large solubility of hydrogen bromide in these solvents, whereby the formation of hydrogen perbromides is facilitated.

Bruner's theory that nuclear substitution is due to ionic bromine is in the main adopted by Bancroft (*loc. cit.*). To account for certain observations, this author finds it necessary, however, to assume that nuclear substitution only occurs when negative bromine ions are present in excess of the corresponding positive ions. Such a condition is brought about by the partial combination of the positive bromine ions with molecular bromine to form complex positive ions, for example, Br_3.

The other view referred to is that put forward by Holleman, who supposes that side-chain substitution is due to molecular bromine, but that substitution in the nucleus is brought about by bromine in the form of hydrogen perbromide, HBr_n. Low temperature and increasing concentration of the solution are favourable to the formation of these polyhalogen compounds, and these are the conditions under which the proportion of nuclear substituted product increases. The fact that nitrobenzene and acetic acid, when added to the toluene, increase the relative amount of the nuclear substitution product, is obviously in agreement with this theory if the solubility relationships, referred to above, are taken into consideration.

An account will now be given of the observations which we have made in connexion with the chlorination of toluene, and the method of analysis of the chlorinated product may be described first.

This product consists of unchanged toluene, *o*- and *p*-chlorotoluene, and benzyl chloride. The benzyl chloride was extracted by Schultze's method (*Ber.*, 1884, **17**, 1675), which consists in boiling a weighed quantity of the liquid with an excess of alcoholic silver nitrate for fifteen to twenty minutes, and weighing the silver chloride. The method was tested with pure benzyl chloride and with benzyl chloride mixed with toluene and *o*- and *p*-chlorotoluene. The following results show that the method of estimation is satisfactory:

0·2618 benzyl chloride gave 0·2983 AgCl; $C_6H_5{\cdot}CH_2Cl = 0·2630$.
0·8220 ,, ,, ,, 0·9192 AgCl; $C_6H_5{\cdot}CH_2Cl = 0·8112$.

The following mixtures were made and analysed:

	I.	II.	III.
Toluene	26·026	3·523	6·459
o-Chlorotoluene	9·328	1·329	4 8765
p-Chlorotoluene	5·306	1·267	2·0575
Benzyl chloride	4·845	2·103	2·3685

I. 6 2013 gave 0·7055 AgCl; $C_6H_5{\cdot}CH_2Cl = 10·04$. Actual = 10·54 per cent.
II. 3·0554 ,, 0·8815 AgCl; $C_6H_5{\cdot}CH_2Cl = 25·46$. ,, = 25·61 ,,
III. 3·4065 ,, 0·5870 AgCl; $C_6H_5{\cdot}CH_2Cl = 15·21$. ,, = 15·03 ,,

The proportion of *p*-chlorotoluene in the mixture was estimated by oxidising the chlorinated product in a sealed tube at 115—120° for five to six hours with nitric acid (one part of acid, D 1·4, and two parts of water). The mixture of acids was collected and washed with cold water. The acids were then boiled with 200 c.c. of water for a few minutes, filtered hot, and washed with a small quantity of boiling water. All the benzoic and *o*-chlorobenzoic acid and a small quantity of *p*-chlorobenzoic acid are thus removed. It was found that one litre of boiling water dissolves about 1·0 gram of *p*-chlorobenzoic acid, so that a loss of approximately 0·20 gram of this acid has to be allowed for in the above method of separation. After washing as described, the acid was dried at 100° and weighed. The melting point of the acid was 234—235°. In carrying out this estimation of the *p*-chlorotoluene, it is necessary to keep the temperature at which the oxidation is effected as low as possible, for otherwise a portion of the *p*-chlorobenzoic acid may be decomposed. Mixtures of the following percentage composition were analysed by the above method:

	I.	II.
Toluene	19·16	15·73
o-Chlorotoluene	43 54	43·07
p-Chlorotoluene	19·40	20 92
Benzyl chloride	17·90	20 28

I. 2·77 gave 0·695 *p* chlorobenzoic acid. *p*-Chlorotoluene = 20·3 per cent.
II. 3·42 ,, 0·880 ,, ,, ,, = 20·8 ,,

In some of the earlier experiments, the total chlorine was determined by the Carius method. By deducting from this the chlorine present as benzyl chloride and *p*-chlorotoluene, the amount of *o*-chlorotoluene was obtained. In the later experiments this method was replaced by a simpler and more rapid process involving the measurement of the density of the chlorinated product. If α, β, γ, and δ are the percentage amounts of toluene, *o*-chlorotoluene, *p*-chlorotoluene, and benzyl chloride respectively in a mixture of these substances, and if d_1, d_2, d_3, and d_4 are the respective densities of these liquids (at 18°), we may obtain α and β from the equations:

$$\alpha+\beta=100-\gamma-\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

$$\frac{\alpha}{d_1}+\frac{\beta}{d_2}=\frac{100}{d}-\frac{\gamma}{d_3}-\frac{\delta}{d_4} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

in which d represents the density of the mixture. This method was applied in the analysis of the following mixtures:

		Percentage composition.		
		I.	II.	III.
Toluene	($d_1=0{\cdot}86791$)	$\alpha=19{\cdot}90$	19·16	15·73
o-Chlorotoluene	($d_2=1{\cdot}08480$)	$\beta=30{\cdot}90$	43·54	43·07
p-Chlorotoluene	($d_3=1{\cdot}07050$)	$\gamma=18{\cdot}64$	19·40	20·92
Benzyl chloride	($d_4=1{\cdot}10271$)	$\delta=30{\cdot}56$	17·90	20·28
Density of mixture		$d_0^{18}=$ 1·03615	1·03584	1·04414
Calculated value of α (per cent.)		19·8	19·0	15·7

In calculating the above values of α, the actual percentage amounts of *p*-chlorotoluene and benzyl chloride were assumed.

Having subsequently ascertained that the ratio of *p*- to *o*-chlorotoluene in the product of chlorination is nearly constant and equal to 1 : 2, the separate estimation of the para-compound was omitted in further experiments, and the total amount of the nuclear substitution product (*o*- + *p*-chlorotoluene) was alone determined. The density of a mixture of the two chlorotoluenes in the above ratio was found to be $d_0^{18}=1{\cdot}0800$. From this and the measured density, d, of a given mixture, we obtain the percentage amounts of toluene (α) and of the mixed chlorotoluenes ($\beta+\gamma$) from the equations:

$$\alpha+(\beta+\gamma)=100-\delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

$$\frac{\alpha}{0{\cdot}86791}+\frac{(\beta+\gamma)}{1{\cdot}0800}=\frac{100}{d}-\frac{\delta}{1{\cdot}10271} \quad . \quad . \quad . \quad . \quad (4).$$

The results obtained for a mixture of known composition by this method are indicated below:

	Percentage composition.
Toluene	α = 92·20
o- and *p* Chlorotoluenes	$(\beta+\gamma)$ = 3·75
Benzyl chloride	δ = 4·05
Density of mixture	d = 0·88250

1·8695 of the mixture gave 0·0868 AgCl, corresponding with $\delta=4{\cdot}10$ per cent. of benzyl chloride. Substituting for δ and d in equations (3) and (4), we obtained $\alpha=91{\cdot}9$, $(\beta+\gamma)=4{\cdot}0$ per cent. This example suffices to show that sufficiently accurate results for the proportion of total nuclear substitution product in the mixture can be obtained by the indirect method of density determination. Previous to the carrying out of the above estimations, the chlorinated mixture was washed with a solution of sodium carbonate until the wash-water, acidified with nitric acid, gave no precipitate with silver nitrate solution. It was then dried over potassium carbonate.

Variations in the Conditions of the Chlorination Process.—In order to ascertain the influence of various factors on the distribution of the chlorine between the side-chain and the nucleus, the following series of experiments were made, the toluene in all cases being heated at its boiling point during the process of chlorination.

Series I *and* II.—Chlorination above a layer of hydrochloric acid solution (D 1·16) in the dark and in diffused daylight.

Series III *and* IV.—Chlorination with moist chlorine in the dark and in diffused daylight.

Series V *and* VI.—Chlorination with dry chlorine in the dark and in diffused daylight.

In the last four series of experiments hydrogen chloride was passed into the toluene with the chlorine, so as to make the conditions correspond as closely as possible with those of series I and II. In the experiments of series V and VI, the gases were passed through concentrated sulphuric acid and then over phosphoric oxide, and the toluene was freshly distilled over sodium.

The results of these experiments are given in table I, in which the last two columns of numbers represent respectively the percentage amounts of chlorine which enter the side-chain and the nucleus. The figures in the third column indicate the extent to which the chlorination was carried in the separate experiments. From a comparison of the individual results in the different series, it would appear that in some cases the distribution of the chlorine between side-chain and nucleus is to some extent dependent on the proportion of the toluene which is actually chlorinated. The variations are, however, not such as to permit of any definite conclusion in regard to this point, and we have considered it permissible to take the mean results of the separate experiments.

TABLE I.

Chlorination with Ordinary Chlorine.

			Percentage of	
Series.	Conditions.	Percentage of substitution products in final mixture.	Benzyl chloride.	*o*- + *p*-Chloro-toluenes.
I. *a*	Layer of hydrochloric acid solution in the dark.	10	16	84
b		10	14·5	85·5
c		10	19	81
d		9	16	84
e		9	17	83
f		9	24	76
g		11	13·5	86·5
h		13	12·5	87·5
	Mean	....	16·5	83·5
II.	Layer of hydrochloric acid solution in the light.	17	64	36
		40	59	41
		48	56	44
	Mean	....	60	40
III.	Moist chlorine and hydrogen chloride in the dark.	12	63	37
		18	46	54
		8	76	24
		9	64	36
	Mean	....	62	38
IV.	Moist chlorine and hydrogen chloride in the light.	50	91	9
		35	90	10
	Mean	....	90	10
V.	Dry chlorine and hydrogen chloride in the dark.	29	91	9
		25	90	10
	Mean	....	90	10
VI.	Dry chlorine and hydrogen chloride in the light.	22	93·5	6·5
		44	94	6
	Mean	....	94	6

In reference to the experiments in series I, certain slight modifications were made in the experimental arrangement in order to ascertain whether the substituting effect of chlorine is influenced by previous exposure to light. In *a* and *b* the chlorine was exposed to the light of an arc lamp, focussed on the wash-bottle containing sulphuric acid, before it came into contact with the toluene. In *c*, *d*, *e*, and *f*, the chlorine was exposed to diffused daylight, the only difference being that in *e* the sulphuric acid in the wash-bottle was replaced by water. In *g* and *h*, the light of an ordinary incandescent electric lamp was allowed to act on the chlorine before it entered the toluene. Although the results of the several experiments vary to some extent, it is not possible to say that the previous light treatment of the chlorine has any definite influence on the proportion of the side-chain substitution.

Before proceeding to compare the data in table I, it will be convenient to present the results of the experiments in which chlorination was effected by chlorine generated by electrolytic decomposition of a concentrated hydrochloric acid solution placed immediately below the toluene. The apparatus used was that described in the previous communication (*loc. cit.*), and, as in the other experiments, the temperature was maintained at the boiling point of toluene.

TABLE II.

Chlorination with Electrolytic Chlorine.

Series.	Conditions.		Percentage of substitution products in final mixture.	Percentage of	
				Benzyl chloride.	*o*- + *p*-Chlorotoluenes.
VII.	In the dark	0·5 amps., 8 hours	9	9·5	90·5
		0·5 ,, 24 ,,	3·5	5·5	94·5
		1 ,, 4 ,,	4	11·5	88·5
		1 ,, 4 ,,	7	8·5	91·5
		4 ,, 1 ,,	10	14·0	86·0
		4 ,, 2 ,,	24	12·0	88·0
			Mean...........	10·0	90·0
VIII.	In the light	1 amp., 4 hours	15	59·0	41·0
		1 ,, 4 ,,	14	69·0	31·0
			Mean...........	64·0	36·0

Examination of table I shows that the influence of light on the ratio of distribution of the chlorine is very pronounced in the case where the reacting chlorine was passed through concentrated aqueous hydrochloric acid in contact with the toluene. The effect of insolation is to raise the proportion of chlorine which enters the side-chain from about 16 to 60 per cent. In the case where the moist gases were passed directly into the toluene, the effect of light is to raise the percentage of benzyl chloride from about 60 to 90. When, however, the dry gases are passed into dry toluene, the proportion of side-chain substitution product obtained in the dark is already so large that any considerable influence of light is impossible. As the numbers show, the effect of light in this case is very slight, the proportion of benzyl chloride being increased from 90 to 94 per cent.

If we compare series I, III, and V, which were all carried out in the dark, it is seen that the distribution of the chlorine is very largely dependent on the amount of water present. In the absence of water, the proportion of benzyl chloride amounts to 90 per cent.; when the chlorine and hydrogen chloride were not dried before passing into the toluene, the mean of the divergent numbers obtained for the proportion of benzyl chloride is only 62 per cent., and when the toluene undergoing chlorination was saturated with water by contact with aqueous hydrochloric acid, the proportion of benzyl chloride is only 16 per cent. The considerable differences in the numbers for the separate experiments of series III may be due to the different amounts of moisture which were introduced by the undried gases in the different experiments.

The data obtained with electrolytic chlorine in the dark (series VII) must be compared with those of series I. The special arrangement adopted in this series was in fact designed to make the conditions as similar as possible to those which obtained in the process of electrolytic chlorination, and thereby to facilitate a comparison of the action of ordinary and electrolytic chlorine. The mean results of the two series are not identical, and it would appear that electrolytic chlorine gives rise to a somewhat smaller proportion of benzyl chloride than chlorine, which is obtained by the action of potassium permanganate on hydrochloric acid. In regard to this difference, it must, however, be noted that the conditions obtaining in the two series of experiments were not quite the same, for in the electrolytic chlorination, hydrogen was continuously evolved from one of the electrodes in the hydrochloric acid solution. It seems probable that the benzyl chloride, which must dissolve to a certain extent in the aqueous solution, is reduced by the nascent hydrogen, and this will result in a smaller proportion of benzyl chloride in the final product.

Series VIII, in which chlorination was effected by electrolytic chlorine in the light, must similarly be compared with series II. The mean values for the proportion of benzyl chloride are approximately the same, and it follows that the action of electrolytic chlorine is not sensibly different from that of ordinary chlorine.

Reference may here be made to the difference in the results which have now been obtained as compared with those communicated in the preliminary note (*loc. cit.*). In the earlier series of experiments, the conditions obtaining in the processes of electrolytic and ordinary chlorination were not sufficiently defined. The electrolytic experiments were made in a badly lighted room, whereas the ordinary chlorinations were effected in good daylight. This is largely responsible for the much greater differences which were found previously for the action of electrolytic chlorine on the one hand, and ordinary chlorine on the other. In the second place, the method previously employed in the analysis of the product of chlorination has been found to be unsatisfactory. This method involved the removal of unchanged toluene by distillation and the oxidation of the residue by means of potassium permanganate. As indicated at the time, the oxidation of the chloro-substitution product by this method is very incomplete, and in the light of later results it appears that the readiness with which the different isomerides undergo oxidation is dependent on their relative proportions in the mixture examined.

The marked influence of moisture on the side-chain nuclear ratio is not peculiar to the chlorination process, for similar effects have been observed in experiments which we have made on the bromination of dry and moist toluene. The bromine used was allowed to remain for some days in contact with potassium bromide, then dried over fused calcium bromide, and distilled over barium oxide. The toluene was freshly distilled over sodium. Fifteen c.c. of a toluene solution, containing 7·2 per cent. by weight of bromine, were introduced into two blackened glass tubes, and 9 milligrams of water were then added to one of the tubes. The preparation of the bromine solution and the filling and sealing of the tubes were effected in a dark room by the aid of a feebly luminous gas flame. The sealed tubes were then placed in a closed box, immersed in a water-bath at 25°, until the bromine had completely disappeared. This occurred in the moist solution after fourteen days, and in the dry solution after thirty days. In a second experiment with a toluene solution containing 8·9 per cent. of bromine, to which in one case 39 milligrams of water were added, fourteen days elapsed before the disappearance of the bromine in the case of the moist solution, the corresponding period for the dry solution being about thirty-five days. The following table gives the relative amounts of side-chain and nuclear substitution products in these experiments:

TABLE III.

		Percentage of	
		Benzyl bromide.	Bromo-toluenes.
Experiment 1	Dry solution.........	27·8	72·2
	Moist ,, ...	18·7	81·3
Experiment 2	Dry solution.........	22·5	77·5
	Moist ,, ...	14·2	85·8

According to these data, the presence of water in the toluene reduces the proportion of benzyl bromide, and at the same time increases the rate at which the bromine disappears. The effect is therefore of the same kind as that observed in the chlorination experiments. On account of the wide differences in the conditions of the chlorination and bromination experiments, it is not, however, possible to make any quantitative comparison of the two series of data.

From a consideration of all the observations relating to the chlorination of toluene, it appears to be established that side-chain substitution is favoured by light, rise of temperature,* and absence of moisture. In so far as these factors are concerned, the chlorination of toluene is influenced in the same way as the bromination process. The two processes would also appear to be similarly influenced by the nature of the medium, for when toluene, mixed with its own volume of nitrobenzene, was chlorinated, an increase in the relative proportion of the nuclear substitution product was observed. No data are available to show the influence of the concentration of the halogen in the case of the chlorination process, and on account of the limited solubility of chlorine in toluene at temperatures at which the reaction takes place, it is doubtful whether the influence of concentration could be experimentally determined with any accuracy.

Independently of the influence of the concentration of the halogen, it is clear that the degree of parallelism between the chlorination and bromination processes is such as to warrant the conclusion that the mechanism of the processes is of the same kind. The more extensive observations relating to the bromination of toluene may therefore be utilised in the elaboration of a general theory of halogenation.

Two theories relating to the special case of bromination have already been referred to in this paper. Both of these offer a plausible explanation of certain facts, but, on the whole, the view that nuclear substitution is due to halogen in the form of polyhalogen compounds appears to be the more acceptable. The diminution in the relative amount of nuclear substitution with rise of temperature and with diminishing concentration of the halogen is consistent with the polyhalogen theory, for both these factors are favourable to the dissociation of the polyhalides. The observed increase in the percentage of nuclear substitution product when certain solvents, such as nitrobenzene, benzonitrile, and acetic acid, are added to the toluene is in accord with the fact that these solvents facilitate the formation of polyhalogen compounds. Observations relating to polyiodides indicate that although these are formed to a small extent in hydrocarbons, carbon tetrachloride,

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* The influence of temperature on the nature of the product of chlorination is shown by experiments which were made with carefully dried materials at 0°. The relative amount of chlorine entering the side-chain was found to be 30 per cent. when chlorination took place in the dark and 45 per cent. when the experiment was conducted in the light. The corresponding numbers, obtained when the toluene was heated at its boiling point, are 90 and 94 per cent. respectively. These results show clearly enough the considerable influence of temperature both in the dark and in the light.

chloroform, and carbon disulphide, they are produced in very much larger quantities in nitrobenzene, ethyl acetate, benzonitrile, acetic acid, and certain other solvents. It is this particular property which appears to determine the nuclear substituting influence of these media.

That similar relationships hold in respect of the formation of polybromides is rendered probable by the results of distribution experiments which were made with carbon tetrachloride and nitrobenzene. According to Bruner and Dluska (*loc. cit.*), the addition of carbon tetrachloride to toluene produces no alteration in the distribution of the bromine between the side-chain and the nucleus; it acts simply as a diluent, and as such reduces the velocity of the reaction.

Fifty c.c. of *N*-aqueous hydrobromic acid were shaken at 18° with 70 c.c. of carbon tetrachloride and of nitrobenzene respectively. After the liquids had been kept for an hour to allow of complete separation, 50 c.c. of the non-aqueous layer were titrated with 0·1*N*-sodium hydroxide. Less than 0·1 c.c. of alkali was required for neutralisation in the case of carbon tetrachloride, and less than 0·25 c.c. in that of nitrobenzene.

The same experiments were then made after the addition of bromine to the hydrobromic acid solution. The amount of bromine added was such that the composition of the resulting solution could be represented by 1·0*N* ($HBr_{1\cdot5}$). After shaking with this solution, 50 c.c. of each of the non-aqueous liquids were treated with potassium iodide and excess of sodium thiosulphate to remove bromine, and then titrated as before with 0·1*N*-alkali. The carbon tetrachloride required, as previously, less than 0·1 c.c. of alkali, whereas the nitrobenzene required 4·4 c.c., which is approximately twenty times * as much as was required in the absence of bromine. These results show clearly the great difference between the two solvents in regard to the formation of polyhalogen hydrogen compounds.

It is possible that the relative stability of polyhalogen compounds in nitrobenzene solution is connected with the ionising power of this solvent, for the solutions of the polyiodides in nitrobenzene have been shown (Dawson and Gawler, Trans., 1902, **81**, 525; Dawson and Jackson, Trans., 1908, **93**, 2063) to be good conductors. Other solvents, like ethyl acetate and benzonitrile, which favour the formation of polyhalogen compounds and increase the relative amount of nuclear product in the bromination of toluene, also yield

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* The correct value of the acid ratio is probably very much greater than this, for a large proportion of the 0·25 c.c. of alkali required for titration in the absence of bromine, is due to the acid character of the nitrobenzene.

solutions which have a high electrical conductivity. Although there is no direct evidence to show that the nuclear substituting effect is conditioned by the ionisation, these facts would seem to indicate that halogen in the form of polyhalogen ion is specially active in this respect.

The fact that solutions of bromine and iodine in moist nitrobenzene are conductors of electricity (Bruner, *Bull. Acad. Sci. Cracow*, 1907, 731) is, at first sight, favourable to the view that nuclear substitution is due to free halogen ions. On the other hand, solutions of chlorine do not conduct (Bruner and Galecki, *Zeitsch. Elektrochem.*, 1910, **16**, 204), and yet the processes of chlorination and bromination appear to be affected in a similar manner when the conditions of the two processes are similarly altered. These facts are difficult to reconcile with the ionic theory of nuclear substitution, and on this account we are inclined to adopt the polyhalogen theory.

Neither this nor the ionic theory appears to offer an immediate explanation of the fact that the presence of water in the toluene increases the relative proportion of the nuclear substitution products. Comparative measurements of the rate of leakage of electricity through dry and moist solutions of chlorine and hydrogen chloride in toluene were made in this connexion, but the results indicate that if there is any difference in the conductivity of the moist and dry solutions, it is not sufficiently large to account for the observed influence of moisture on the chlorination process on the assumption that nuclear substitution is due to chlorine ions. In so far as the resultant effects are concerned, the action of moisture is opposed to that of light, for this increases the rate of side-chain substitution, and the former accelerates the process of nuclear substitution. Before these catalytic effects can be explained, further experiments are necessary.

The question of carriers may finally be discussed. The assumption that the activity of these substances is due to an increase in the concentration of halogen ions as a consequence of the formation of more highly ionised "carrier-halogen" compounds is not, so far as we are aware, supported by any experimental evidence. On the other hand, if such "carrier-halogen" compounds are themselves of the nature of perhalogen compounds, or if they are capable of combining with further quantities of halogen to form such perhalogen derivatives, the formation of nuclear substitution products in the presence of carriers is explicable in terms of the polyhalogen theory without the necessity of formulating any additional electrolytic hypothesis. From a consideration of the valency relationships of the various substances which serve as carriers, it seems likely that all these substances are capable of forming dissociating halogen addition compounds which belong to the polyhalogen type.

In the course of the above experiments, we have observed certain colour phenomena in connexion with the process of chlorination, which we propose to reserve for a further communication. When moist chlorine is passed into boiling toluene in the light, the toluene gradually assumes the yellow colour of chlorine. If, however, hydrogen chloride is passed in simultaneously, the yellow colour disappears, reappearing when the hydrogen chloride is cut off. In the dark the liquid retains its yellow colour in presence of hydrogen chloride. In some cases the chlorination product, after carefully washing free from chlorine and hydrogen chloride, retains a permanent pale yellow colour. The exact conditions which are necessary for the production of the colour change, which is probably due to the formation of a small quantity of a yellow-coloured substance, have not yet been determined.

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