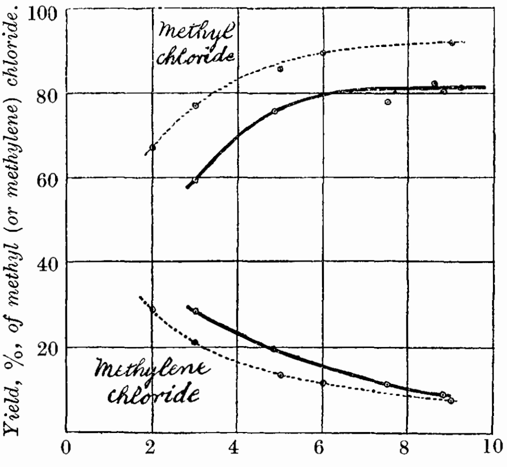
CCCXII.—*Thermal Chlorination Reactions in the Gaseous Phase, with Short Heating Periods.*

By JOHN MASON and THOMAS SHERLOCK WHEELER.

A REVIEW of the literature on the thermal chlorination of methane showed that there was a region of experimental conditions not already investigated, *viz.*, high reaction tube temperatures, no catalyst, and very short heating periods, *i.e.*, rapid passage of the gases through the heated chamber. This method of working has a two-fold advantage : (i) it requires only a minimum of material in the reaction vessel at any moment, and (ii) since very high gas velocities are used, it minimises the risk of explosion where this is probable. It was therefore decided to study the effect of these conditions. The method having been found unsuitable for the complete chlorination of methane to carbon tetrachloride, it was subsequently investigated from the standpoint of controlled chlorination to methyl chloride and thence to methylene chloride. It was further applied, with suitable tube temperatures, to the reaction propane ⟶ *n*- and *iso*-propyl chlorides. The method has also been successfully applied to the chlorination of benzene and toluene, but these applications are not included in the present paper.

The chlorination of methane, and bimolecular stage reactions in general, have been investigated theoretically by Martin and Fuchs (*Z. Elektrochem.*, 1921, **27**, 150), with whose conclusions the results obtained in the present work were compared. In the case of methane the following formulæ are given for the final concentrations of methyl and methylene chlorides in the product, *A* and *B* being the fractions by volume of methane and chlorine respectively in the initial mixture.

FIG. 1.



Vols. of methane per vol. of chlorine.

Continuous curves = experimental values.
Broken curves = theoretical values (from formulæ of Martin and Fuchs).

$$[CH_3Cl] = B(4A - B)^3/64A^3$$
$$[CH_2Cl_2] = 3B^2(4A - B)^2/128A^3$$

From these, the theoretical percentage yields of the two compounds on input chlorine were calculated. Corrections were applied to the experimental values on the assumption that any missing chlorine represented lost methyl chloride, and in Fig. 1 the figures are compared graphically with the values from the formulæ. The experimental and the theoretical curves are similar in form, but the methyl chloride yield remains about 10% below the theoretical value. The methylene chloride values are slightly higher than required by theory, but the curve approaches the theoretical one as the methane : chlorine ratio increases. For plotting the experimental curves, the maximum and the minimum yields respectively of methyl and methylene chloride were taken. In addition to these complete equilibrium formulæ, obtained only for the four-stage process involved in methane chlorination, general kinetic formulæ are given for any reaction involving n bimolecular stages. In these no account is taken of reverse reactions, and the rate of reaction of a hydrocarbon or partially substituted hydrocarbon molecule is assumed to be proportional to the number of available hydrogen atoms. The general formula giving the percentages of initial substance (*e.g.*, methane) converted into the mth product, in terms only of the total percentage consumed (x), is

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

In the chlorination of methane, propane, and methyl chloride, the experimental values were compared respectively with the theoretical ones for 4-, 8-, and 3-stage processes (Tables III, IV, V), with fairly good agreement in each case for the first stage of the reaction. The calculations were made on the corrected chlorine balances.

EXPERIMENTAL.

(1) *The Action of Chlorine on Methane.*

Methane (96—99%) and chlorine, after passing respectively through a gas-meter and a calibrated flow-meter, were passed at the required rates into the reaction tube, *via* three-way taps and a Y-piece. The gases were obtained from cylinders and were not specially dried. The reaction tubes, of stated diameter, were of a special alumina–silica refractory supplied by the Morgan Crucible Company. The tube was heated electrically in a suitable furnace, the heated length being *ca.* 15 cm. The tube temperature (external) was measured by a platinum–rhodium thermocouple reaching to the mid-point of the furnace. The reaction tube was so arranged that the gases entered the heated length as soon as possible after being mixed. On the exit side, after preliminary cooling in a 1-litre ice-cooled flask, the gases passed through three Drechsel wash-bottles, the first two containing water to remove hydrogen chloride, and the third 20% caustic soda solution to remove unchanged chlorine. Then, after passing up a calcium chloride drying-tower, the gases entered freezers cooled by solid carbon dioxide–ether mixture and liquid air, for the condensation of chloro-derivatives and excess methane. In previous work − 110° is the lowest temperature used for condensation. A gas-meter was included after the freezers for the measurement of any uncondensed methane, and suitable arrangements were made for taking gas samples, usually at a point between the carbon dioxide–ether and the liquid-air freezers.

The percentages of input chlorine (i) converted into hydrogen chloride and (ii) passing through unchanged were determined by titration of the washer liquids. The chloro-compounds were fractionated as follows: methyl chloride was boiled off up to 0°, and the remaining mixture (methylene chloride, etc.) fractionated from a distillation flask, cuts being taken at approximately the mid-point temperatures, as recommended by Young (" Distillation Principles and Processes," p. 170). In the experiments of Table I the liquid methyl chloride was estimated approximately by a volume method, but as this gave low results, the method of direct weighing was adopted in later experiments (Table II), a vessel designed to withstand the vapour pressure at the ordinary temperature being used.

Table I contains examples of the results obtained with tube temperatures of 1200—1400°, and very high space velocities. This term (S.V. in tables) is defined as the number of volumes of gas, at reaction-tube temperature, passing through the heated volume per minute. The period of heating, in minutes, is therefore the reciprocal of the space velocity. When packed tubes were used, the figures were corrected approximately for the volume of the packing—in all cases of the same material as the tube itself. As will be seen, it has been found possible to work with periods of heating less than 0·001 min., and to obtain high outputs with relatively small apparatus.

At the high temperatures used, appreciable amounts of acetylene and hydrogen, along with small amounts of ethane and ethylene, were obtained in the exit gases. Carbon and tar (containing hexachloroethane, naphthalene, etc.) were formed in these experiments, increasing in amount with tube temperature and proportion of chlorine in the initial mixture. The percentage yields of chloro-compounds were calculated throughout on input chlorine; it was found very difficult to obtain satisfactory readings for unused methane. As would be expected, the percentage of chlorine coming through unchanged (at the same space velocity) increases as the proportion of methane increases. The formation of acetylene is to be expected when methane is subjected to the action of an intense energy field, here set up by the temperature of the furnace and by the heat of reaction.

In Expt. 7, oxygen (0·2 vol.) was passed in with the reaction mixture. Oxidation of methane to formaldehyde took place, and the chlorine was recovered almost quantitatively as hydrogen chloride; in the exit gases there was 15·8% of carbon monoxide.

TABLE I.

Experiments with Excess of Methane.

				Washer analyses (% of Cl_2 input).		Yields (% on Cl_2 input) of			
Expt.	S.V.	$Cl_2 : CH_4$.	Temp.	Cl_2.	HCl.	CH_3Cl.	CH_2Cl_2.	$CHCl_3$.	CCl_4.
17	30,800	1 : 1·5	1400°	0·005	88·5	17	(Higher products not fractionated)		
19	30,700	1 : 1·5	1400	0·01	89·1	17·1	7·9	1·3	1·5
29	11,900	1 : 3	1200	Nil	72·2	33·6	16·4	2·1	0·9
26	23,900	1 : 2	1200	2·5	56·6	35	21·1	3·3	0·7
25	24,300	1 : 3	1200	0·7	56·7	28·4	31·3	3·2	1·8
30	23,800	1 : 3 *	1200	22·1	44·3	26	19·2	3·7	5·5
27	23,800	1 : 5	1200	8·0	55·6	37·5	21·2	2·4	1·9
28	23,800	1 : 7	1200	14·0	50·4	39·2	13·4	2·0	2·0
7	26,100	1 : 1·5 †	1400	Nil	92·1	(Traces of liquids smelling of formaldehyde in freezers.)			

* Plus water vapour. † Plus 0·2 vol. of oxygen.

In the above experiments the amount of product boiling up to 0° (up to room temperature in Expt. 17) was taken as methyl chloride, and the fractions of the residue boiling (1) up to 51°, (2) at 51—66°, (3) at 66—95°, were taken as methylene chloride, chloroform, and carbon tetrachloride, respectively. There was, in some cases, a slight residue above 95°, consisting probably of more complex chloro-compounds. Correction for any methylene chloride in the crude methyl chloride was made (except in Expt. 17) by redistillation to 0°, any residue being taken as methylene chloride. Any loss on distillation of the higher products was taken as methylene chloride.

It appears that to obtain the maximum yield of chloro-compounds, even though high space velocities are used, the tube temperature must not be so high as to cause pyrolysis. For later experiments, therefore, temperatures of 800—900° and lower space velocities were used (1 cm. diameter tube). Preliminary experiments were first carried out to find suitable working conditions—shown by values for hydrogen chloride in the washers only slightly more than 50%, indicating negligible pyrolysis, and by low values for unreacted chlorine. The opportunity was taken to effect several improvements in technique. The effect of losses in the apparatus was eliminated by condensing the products for a definite time in the middle of the experiment, after an initial period long enough for the washers to become saturated with methyl chloride, etc. The methyl chloride was weighed, and the fractionation methods were improved, the methylene chloride fraction being taken up to 49° only. When working with packed tubes, special calibrations of the gas-meter and flow-meter were made, at the same back-pressures as obtained in the various experiments. In this series of experiments chlorine : methane ratios from 1 : 3 to 1: 9 were used. When the excess of methane exceeded the former value, loss of methyl chloride occurred during the fractionation of this substance from the condensed methane. To prevent this, the use of silica or iron oxide gel cooled in carbon dioxide–ether (compare Taylor, D.S.I.R. Report, C.R.B. 4/3/7) was successfully introduced. Typical experimental results are given in Table II. In the exit gases with conditions as in Expt. 11 there was no acetylene. When a large excess of methane was being used (1 : 5 and above), the main product boiling above 0° was assumed to be methylene chloride; that this was a justifiable assumption was shown by satisfactory chlorine balances being obtained after the introduction of the use of silica or iron oxide gel (Expts. 8, 10, 11, and 12).

It was advantageous to use packed tubes in these experiments (and also in the chlorination of methyl chloride and propane), since complete reaction could be obtained with a much larger flow of reaction mixture, and pyrolysis was negligible at the temperatures used. A mercury manometer was used to determine back-pressures.

TABLE II.

Action of Chlorine on Methane (Second Series).

Expt.	3.	5.	6.	7.	8.	10.	11.	12.
Temp.	850°	900°	900°	900°	900°	900°	900°	900°
S.V. (min.$^{-1}$)	2107	9400	9400	9300	5700	5600	8100	9100
Ratio, $Cl_2 : CH_4$	1 : 3	1 : 2·97	1 : 4·85	1 : 8·8	1 : 8·6	1 : 8·4	1 : 7·5	1 : 9·2
Input CH_4 (l./min.)	4·79	12·73	14·18	15·21	14·8	14·5	12·95	15·0
,, Cl_2 (,,)	1·583	4·285	2·922	1·729	1·729	1·729	1·729	1·631
% of input Cl_2 in washers as Cl_2	0·34	Nil	0·05	0·097	0·16	0·12	0·16	0·14
as HCl	53·02	54·74	52·2	51·0	51·35	51·2	51·61	50·5
Yield of CH_3Cl (%, on Cl_2 input)	41·1	48·3	50	42·5	82·1	70·5	75·6	72·6
Cl_2 balance (% of input):								
CH_3Cl	20·26	24·11	24·98	21·28	41·1	35·22	37·78	36·3
CH_2Cl_2	17·14	14·17	9·86	4·46	9·7	8·39	5·58	6·46
$CHCl_3$	1·61	1·43	—	4·35	—	5·0	3·66	2·35
CCl_4	1·91	—	—	—	—	—	—	—
Total in washers	53·4	54·7	52·3	51·1	51·5	51·3	51·8	50·6
Total balance	94·3	94·5	87·1	81·2	102·3	99·9	98·8	95·8
Yield % of CH_3Cl (calc. on 100% Cl_2 balance)	52·7	59·3	75·8	80·2	—	—	77·8	81·2
Back-press. (in. of Hg)	0·3	3·6	2·8—3·2	3	3	3	3—3·2	3—3·2

Notes.

Expt. 3. Slight pyrolysis. Faint deposit in first washer. Smell of C_2Cl_6. Fractionation from distillation flask.

Expt. 5. No pyrolysis. 6-Pear Young column used in fractionation.

Expt. 6, 7, 8, 10, 11, *and* 12. No pyrolysis. Portion above 0° assumed to be CH_2Cl_2. Liquid in ice-cooled flask taken as $CHCl_3$ for purposes of chlorine balance.

Expts. 8 *and* 10. Silica gel, cooled in carbon dioxide–ether, used.

Expts. 11 *and* 12. Iron oxide gel, similarly cooled, used.

In the experiments of Table II, methyl chloride was boiled off up to room temperature. Correction was applied for any methylene chloride in the crude methyl chloride by evaporating off the latter up to 0° and weighing the residue. The methylene chloride fractions of Expts. 3 and 5 were respectively up to 49° and 47·5°. Any loss on distillation of the higher products was counted as methylene chloride. In Expt. 3 the fraction 49—56·5°, and in Expt. 5 the residue above 47·5°, were taken as chloroform. The " carbon tetrachloride " of Expt. 3 represents residue above 56·5°, plus a correction for any liquid in the ice-cooled flask.

In Table III the results of the experiments of Table II are compared with the theoretical values calculated from the kinetic formulæ of Martin and Fuchs (p. 2284) for a four-stage process (*i.e.*, $n = 4$). The agreement for methyl chloride is good.

TABLE III.

	Expt. 3.		Expt. 5.		Expt. 6.		Expt. 7.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
CH_4 chlorinated, % of total	23·9	—	25·2	—	17·6	—	9·96	—
% converted into CH_3Cl ...	17·4	21·5	20·0	22·5	15·6	15·6	9·1	9·6
% ,, ,, CH_2Cl_2 ...	5·8	2·3	4·8	2·5	2·0	1·1	0·51	0·38
% ,, ,, $CHCl_3$	0·36	0·11	0·45	0·13	—	0·04	0·35	0·007
% ,, ,, CCl_4	0·32	0·002	—	0·002	—	0·0004	—	—
	Expt. 8.		Expt. 10.		Expt. 11.		Expt. 12.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
CH_4 chlorinated, % of total	10·7	—	9·8	—	11·5	—	9·7	—
% converted into CH_3Cl ...	9·6	10·2	8·4	9·4	10·4	10·95	8·8	9·4
% ,, ,, CH_2Cl_2 ...	1·13	0·44	1·0	0·37	0·74	0·51	0·70	0·36
% ,, ,, $CHCl_3$ ...	—	0·0084	0·4	0·006	0·33	0·011	0·17	0·006
% ,, ,, CCl_4	—	—	—	—	—	—	—	—

(2) *The Action of Chlorine on Propane.*

Similar experiments were carried out with propane, obtained from a cylinder fitted with a suitable valve. The mode of procedure was similar to that in the final experiments with methane, except that cooling by ice–salt and solid carbon dioxide–ether freezing mixtures was found sufficient for condensation of the products. The separation of propane from the resultant mixtures was performed similarly to that of methyl chloride in the preceding section.

The b. p.'s of propane and its two monochloro-derivatives are : propane − 38°, *iso*propyl chloride 37°, *n*-propyl chloride 46°. On fractionation of the mixture of chloro-compounds after removal of the propane, a cut was taken at 41·5°, and the process stopped at 72·5°—the mid-point temperatures, as recommended by Young (*op. cit.*), a correction being applied for losses. The first fraction was usually larger than the second, suggesting that more of the *n*- than of the *iso*-compound was formed. The percentage yields given (on chlorine) represent both chloro-compounds. Examples of the results are in Table IV. The probable yield of propyl chloride in Expt. 1 was approx. 88%. Any residue above 72·5° was taken as propylene chloride for the purpose of chlorine balance. Low chlorine balances were caused by loss of chloro-compounds (probably the monochloro-derivatives) during the evaporation of the propane, the prevention of which could only be accomplished by the use of more elaborate fractionation technique. Percentage yields of propyl chloride corrected for chlorine balance are given in addition to the actual figures obtained. In Table IV, the results are compared with values from Martin and Fuchs's kinetic formula for an 8-stage process ($n = 8$), with good agreement for propyl chloride.

TABLE IV.

Action of Chlorine on Propane.

(1 cm. tube, 15 cm. heated length, empty.)

	Expt. 1.	Expt. 2.
Temp.	700°	700°
S V. (min.$^{-1}$)	960	795
Ratio, $Cl_2 : C_3H_8$	1 : 6·2	1 : 5
Input C_3H_8 (l./min.)	2·89	2·31
,, Cl_2 (,,)	0·466	0·466
% of input Cl_2 in washers { as Cl_2	Trace	Nil
as HCl	55·9	60·4
Yield of C_3H_7Cl (% on Cl_2 input)...	56·6	56·8
Cl_2 balance (% of input) :		
C_3H_7Cl	28·3	28·39
$C_3H_6Cl_2$	—	2·32
Total in washers	55·9	60·4
Total balance	84·2	91·1
Yield of C_3H_7Cl (% calc. on 100% chlorine balance)	88·2	74·6
Back-press. (in. of Hg)	—	—
Notes	Only small amount of liquid above 48·5°; taken as entirely propyl chlorides.	

Calculations from formula (p. 2284) *with* n = 8.

	Obs.	Calc.	Obs.	Calc.
C_3H_8 chlorinated, % of total	14·2	—	15·6	—
% converted into C_3H_7Cl	14·2	13·3	15·1	14·4
% ,, $C_3H_6Cl_2$	—	0·9	0·48	1·07

(3) *The Action of Chlorine on Methyl Chloride.*

The high space-velocity method was similarly applied to the chlorination of methyl chloride to methylene chloride, on which reaction little work has been published (I.G., B.P. 283,119; F.P. 646,661).

The experimental methods were as in the later experiments with methane. The gas-meter was replaced by a flow-meter calibrated to deliver methyl chloride, obtained from a cylinder fitted with a connector valve as used on the chlorine cylinder. Preliminary experiments showed that it was impracticable to work with tube temperatures as high as had been used with methane owing to pyrolysis, resulting in the formation of undue amounts of hydrogen chloride, and also hexachloroethane, naphthalene, carbon, etc. (Hurd, " Pyrolysis of Carbon Compounds," p. 125; Wiesler, *Chem.-Ztg.*, 1928, **52**, 182). Suitable conditions were found for the final experiments, the weighing of methyl chloride, the elimination of effect of losses in the apparatus, and the corrections for back-pressure (as described under methane) being used. In this case condensation of the products was much easier than in the experiments with methane : two freezers cooled by solid carbon dioxide–ether were sufficient, but an extra one in liquid air was always added to ensure complete recovery.

The method of fractionation used for the experiments of Table V was as follows : Excess of methyl chloride was allowed to boil off up to room temperature, the distillate being recondensed in a vessel cooled in carbon dioxide–ether (the freezer designed for weighing methyl chloride); correction was applied for any methylene chloride in the crude methyl chloride by evaporating off the latter up to 0°, and weighing the residue. For the higher products, the portions of liquid were transferred to a distillation flask, weighed, and fractionated, the fractions being : up to 51°, 51—66°, 66—95°, and residue. Any liquid in the ice-cooled flask of the chlorination apparatus was suitably treated; when the freezers were only included for a part of the total time, the liquid was fractionated separately, and a proportionate correction applied. The methylene chloride fraction was distilled into a vessel cooled in carbon dioxide–ether, and any loss on distillation was counted as methylene chloride; if this fraction was taken to 51°, high values for methylene chloride were obtained. A correction determined by the fractionation of known mixtures was applied to the data of Expts. 33, 34, and 37. No correction was necessary in Expts. 36, 38, and 39, for in each case nearly all of the 51°-fraction boiled below 45° (97·5% in Expt. 39). No pyrolysis was detected in any of these six experiments (Table V).

In Table VI the results are compared with values from Martin and Fuchs's kinetic formula for a three-stage process, with good agreement for methylene chloride.

The Pyrolysis of Methyl Chloride.—Experiments were carried out on the pyrolysis of methyl chloride alone, with experimental conditions similar to those of the chlorination experiments (1-cm. diameter tube, packed, heated length 30 cm., tube temperature 600°). The results are in Table VII. The amount of pyrolysis was measured by the hydrogen chloride formed, which was removed by water washers and determined by titration with standard caustic soda, with phenolphthalein as indicator. The inputs of methyl

TABLE V.

Action of Chlorine on Methyl Chloride.

(1 cm. tube, 30 cm. heated length, packed.)

Expt.	33.	34.	37.	36.	38.	39.
Temp.	600°	600°	600°	600°	600°	600°
S.V. (min.$^{-1}$)	2990	2990	2990	1990	1990	1660
Ratio, $Cl_2 : CH_3Cl$	1 : 2·7	1 : 2·7	1 : 2·7	1 : 4	1 : 4	1 : 5·4
CH_3Cl input (l./min.)	10·67	10·67	10·67	7·8	7·8	6·87
Cl_2 input (l./min.)	3·985	3·985	3·985	1·951	1·951	1·271
% of input Cl_2 in washers, as Cl_2	Nil	Nil	Nil	Trace	Trace	0·058
% of input Cl_2 in washers, as HCl	49·4	49·8	49·2	51·4	51·9	51·8
Yields % of CH_2Cl_2 :						
on Cl_2 input	71·1	76·2	71·2	91·1	91	93·1
on CH_3Cl consumed	80	83·1	79	80·7	80·5	83
Cl_2 balance (% of input) :						
CH_2Cl_2	35·64	38·18	35·7	45·5	45·5	46·7
$CHCl_3$	13·77	9·8	10·0	3·37	3·58	0·2
CCl_4	—	—	—	—	—	—
Total in washers	49·4	49·8	49·2	51·4	51·9	51·8
Total balance	98·8	101·7	98·9	100·2	100·9	98·7
Yield % of CH_2Cl_2 (on 100% Cl_2 balance)	73·7	—	73·7	—	—	96
CH_3Cl balance (% of input) :						
Recovered	66·7	65·7	66·2	72	71·8	79·2
CH_2Cl_2	26·6	28·6	26·6	22·8	22·7	17·2
$CHCl_3$	4·3	5·2	3·7	0·85	0·89	0·04
CCl_4	—	—	—	—	—	—
Total balance	97·6	99·4	98·1	95·7	95·4	96·6
Back-press. (in. of Hg)	6·5	6·5	6·5	2·9	2·9	2·0

TABLE VI.

	Expt. 33.		Expt. 34.		Expt. 37.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
CH_3Cl chlorinated, % of total	32·7	—	32·1	—	31·4	—
% converted into CH_2Cl_2	27·6	28·9	28·5	28·1	27·6	27·5
% ,, ,, $CHCl_3$	5·2	4·1	3·7	3·9	3·8	3·7

	Expt. 36.		Expt. 38.		Expt. 39.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
CH_3Cl chlorinated, % of total	23·6	—	23·7	—	17·84	—
% converted into CH_2Cl_2	22·8	21·5	22·8	21·6	17·8	16·7
% ,, ,, $CHCl_3$	0·84	2·0	0·9	2·0	0·04	1·13

TABLE VII.

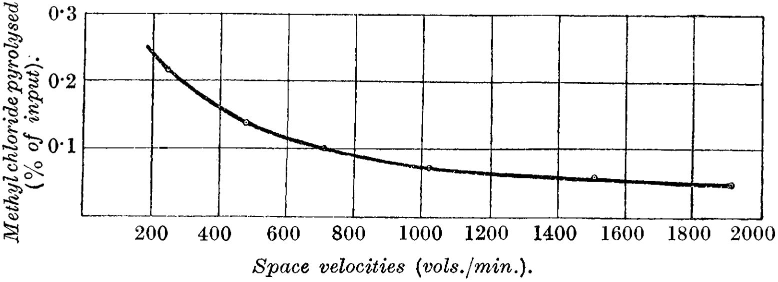
Pyrolysis of Methyl Chloride.

Expt.	Temp.	Input CH_3Cl (litres/min.).	Space velocity (min.$^{-1}$).	CH_3Cl pyrolysed, % of input.
1	600°	9·36	1910	0·0497
2	,,	7·6	1550	0·0595
3	,,	5·0	1020	0·0741
4	,,	3·46	706	0·1012
5	,,	2·32	473	0·1392
6	,,	1·19	242	0·2160

chloride were checked, at the correct back-pressures. To avoid the vitiating effect of residual traces of hydrogen chloride in the apparatus, the run was allowed to proceed, in each determination, for some minutes before connexion to the washers was made, and the apparatus was washed out with nitrogen between successive runs.

The results of Table VII are expressed graphically in Fig. 2. It will be seen that pyrolysis of methyl chloride alone is negligible with these conditions. At the space velocities of Expts. 36, 38, and 39, the extent of pyrolysis is 0·05—0·06% of input. Pyrolysis in chlorination processes is probably largely determined by the thermal effect of the reaction.

FIG. 2.



Summary.

A high space velocity method, with high reaction-tube temperatures, has been developed for controlled chlorination in the gaseous phase. Tubes of a special refractory were used, either empty or (preferably) packed with pieces of the same material.

Even with high rates of flow, pyrolysis occurs if the tube temperature is too high, and to obtain the best results the conditions must be adjusted to avoid this. In the first experiments with methane, with temperatures of 1200—1400° and space velocities of 10,000—31,000 vols. per min., there was considerable pyrolysis, especially if the reaction mixture contained only a small excess of methane.

With a lower temperature (900°), an excess of methane, and suitable space velocities, the method is efficient for the production of methyl chloride, with small amounts of methylene chloride. The results were compared with the values given by the complete equilibrium and kinetic formulæ of Martin and Fuchs. The latter formulæ gave fair agreement for methyl chloride. Yields of this product up to approx. 80% (on chlorine input) were obtained.

The chlorination of propane was similarly investigated. Of the two monochloro-compounds, *n*-propyl chloride appeared to be formed in larger amount. On comparison with values given by the kinetic formulæ for an 8-stage process, good agreement for this first stage was obtained.

In the chlorination of methyl chloride, the yields of methylene chloride on chlorine input were slightly above 90%, and were in agreement with the kinetic equations for a three-stage process. With conditions similar to the final experiments it was shown that the pyrolysis of methyl chloride alone was very slight.

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