708. *Photochlorination. Part II. The Photochlorination of Methane.*

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The photoreaction between chlorine and methane has been examined under different intensities of absorbed light of wave-lengths 3650 and 4060 A., and at various pressures of methane, chlorine, and of the added gases oxygen, hydrogen chloride, nitrogen, and argon.

The inhibiting action of oxygen was extreme.

For oxygen-free mixtures, the quantum efficiency tended to approach inverse proportionality to the square root of the absorbed light intensity at low intensities, but at high intensities became independent of the absorbed light intensity; it was directly proportional to methane pressure at low pressures, but approached a constant maximum at high pressures; it was decreased by the addition of argon, nitrogen, and hydrogen chloride, and increased to a maximum at an intermediate pressure of chlorine.

Quantum efficiency values at high light intensities were of the order 2×10^3 for pressures of methane and chlorine of 45 mm.

The observations are interpreted by a chain mechanism in which chain ending involves the formation of Cl_3 molecules.

Many analogies can be drawn between the chemical behaviour of hydrogen and methane; in particular, they both react with chlorine to give the corresponding chlorides, and on illumination by light absorbed by the chlorine the reaction in both cases is very rapid, proceeding by a chain mechanism of high quantum efficiency. In spite of exhaustive investigation of the hydrogen–chlorine photo-combination, there is still doubt as to the means by which chlorine atoms are removed in the gas-phase chain-ending process, the reaction being complicated by surface action, diffusion of chain carriers, and possibly by convection; on the other hand, comparatively little examination has been made on similar lines of the corresponding reaction with methane.

Such photo-reaction produces in general, in addition to hydrogen chloride and methyl chloride, the further substitution products methylene dichloride, chloroform, and carbon tetrachloride. Coehn and Cordes (*Z. physikal. Chem.*, 1930, *B*, **9**, 1) found the quantum efficiencies of production of each of these species to be of the same order of magnitude; in the case of methane, the value of the quantum efficiency, on initial exposure to light, was approximately 2×10^4, when the proportion of methane to chlorine was 1 : 1. No chloroethanes were detected. The chain mechanism preferred was that involving CH_3 radicals, a conclusion also supported by Jones and Bates (*J. Amer. Chem. Soc.*, 1934, **56**, 2282), who used a flow system in which, however, small amounts of oxygen were present, and by Tamura (*Rev. Phys. Chem. Japan*, 1941, **15**, 86).

In Tamura's experiments the only variable was the intensity of the incident light; on the basis of three such values, the rate was found to be proportional to a power of the absorbed light ($I_{abs.}$) approaching 0·5, this leading to the conclusion that reaction chains were terminated mainly by mutual recombination of chain carriers rather than by inhibitors or on the walls of the containing vessel. Calculation of the mean life of a chlorine atom, by a method of thermal analysis of the reaction rate, then showed that the direct mutual recombination of chlorine atoms in a triple stabilised collision was not of importance; the reaction scheme favoured involved the species Cl_3 as an unstable intermediate.

The results of an investigation into the corresponding photo-combination of hydrogen and chlorine (Ritchie and Taylor, *Proc. Roy. Soc.*, 1942, *A*, **180**, 423) have been interpreted by a similar mechanism. A comparable study of methane photochlorination has now been carried out, in which the effects, on the quantum efficiency, of the variation of absorbed light intensity, and of different pressures of chlorine, methane, oxygen, nitrogen, argon, and hydrogen chloride have been examined.

EXPERIMENTAL.

The general method of experiment was as described by Ritchie and Taylor (*loc. cit.*) (cf. Ritchie and Norrish, *Proc. Roy. Soc.*, 1933, *A*, **140**, 99), in which the photo-reaction rate was measured photometrically by light of wave-length 3650 A., after sufficient oxygen had been added to reduce the rate to negligible proportions. The cylindrical reaction vessel was of transparent silica, of approximate volume 30 ml., pressures being measured by a balanced Bourdon gauge system. To obtain reproducible rates, every care was necessary, not only in the purification of reactants but also in all working procedures.

Cylinder methane, after preliminary purification by sodium hydroxide, concentrated sulphuric acid, and phosphoric oxide, was subjected to repeated fractional distillation by means of liquid oxygen, and finally passed through molten sodium. The reaction rate was very sensitive to oxygen and the sodium treatment could not be omitted; a similar purification was given to nitrogen and argon. Electrolytic hydrogen, used for the production of hydrogen chloride *in situ* in the reaction vessel, was passed over hot copper, platinised asbestos, and finally over a white-hot tungsten filament, with suitable liquid-oxygen traps for any water produced. Cylinder chlorine was purified by repeated fractionation; and every precaution was taken to prevent oil vapour from the Hyvac oil pump or mercury vapour from the balancing mercury column of the Bourdon gauge from reaching the reactant gas streams or the reaction vessel. With extensive washing out of the system with the reactants and by pre-illumination of the chlorine as finally introduced, the initial pressure rise on illumination could be taken as a good indication of the ultimate reproducibility of an experiment.

To minimise progressive chlorination, times of illumination were as short as experimentally permissible. The change in chlorine pressure was usually not greater than 10 mm., for initial chlorine pressures of 50 mm. Variation in reproducibility of rate results was normally within 10%. Absolute values of quantum efficiency (γ) of chlorine removal were obtained by calibration of the light intensity in terms of the rate of hydrogen chloride formation for $[H_2] = [Cl_2] = [O_2] = 50$ mm., pressures for which the quantum efficiency has already been established under comparable conditions (Norrish and Ritchie, *loc. cit.*, p. 713). The source of light used in all series except one (see Table II*b*) was a 125-watt, 230 v. A.C. Osira mercury-vapour lamp run in conjunction with a voltage stabiliser. Combinations of filters and blue glass plates were employed to reduce the intensity of the light beams of wave-length 3650 and 4060 A. All experiments were carried out at 25°; at this temperature no reaction in the absence of light was ever observed over times comparable to those involved in the photo-reaction.

Results.—

TABLE I.

Variation of oxygen pressure.

(*a*) $\lambda = 3650$ A. $[Cl_2] = [CH_4] = 45$ mm. $[HCl] = [CH_3Cl] = 5$ mm.
Mean $I_{abs.} = 7 \cdot 9 \times 10^{13}$ quanta/sec.

$[O_2]$, mm.	t, secs.	$I_{abs.}$ (scale divs.).	$\gamma \times 10^{-3}$.	$[O_2]$, mm.	t, secs.	$I_{abs.}$ (scale divs.).	$\gamma \times 10^{-3}$.
0	35	10·2	2·2	3·0	1200	10·4	0·049
0·1	80	10·3	0·91	6·0	3000	10·2	0·026
0·25	120	10·4	0·52	10·0	7200	10·0	0·015
1·0	600	10·2	0·15				

(*b*) $\lambda = 3650$ A. $[Cl_2] = [CH_4] = 45$ mm. $[CH_3Cl] = 5$ mm. $[HCl] = 210$ mm.

$[O_2]$, mm.	t, secs.	$I_{abs.}$ (scale divs.).	$\gamma \times 10^{-3}$.
6·0	3000	10·2	0·027

TABLE II.

Variation of light intensity.

$[Cl_2] = [CH_4] = 45$ mm. $[HCl] = [CH_3Cl] = 5$ mm.

λ, A.	*t*, secs.	$I_{\text{abs.}} \times 10^{-13}$.	$\gamma \times 10^{-3}$.	λ, A.	*t*, secs.	$I_{\text{abs.}} \times 10^{-13}$.	$\gamma \times 10^{-3}$.
(*a*) Intermittent light source (230 v., A.C.).							
3650	40	7·9	2·02	3650	420	0·757	2·54
3650	40	7·9	2·20	3650	600	0·402	2·73
3650	40	7·9	2·14	4060	800	0·277	3·52
3650	80	4·48	2·37	4060	1000	0·174	4·56
(*b*) Continuous light source (100 v., D.C.).							
3650	40	14·1	1·55	3650	600	0·61	2·13
3650	40	13·8	1·63	4060	800	0·35	2·27
3650	70	8·25	1·41	4060	1200	0·17	2·83
3650	420	1·29	1·64	4060	3600	0·046	2·98

(*c*) $\lambda = 3650$ A. $[O_2] = 10·1$ mm.

$[H_2]$, mm.	$[Cl_2]$, mm.	*t*, secs.	ΔCl_2, mm.	$I_{\text{abs.}} \times 10^{-13}$.	γ_{HCl}.
42·8	42·8	240	14·5	22·2	560
42·1	42·1	480	15·8	11·9	567
42·6	42·6	2400	14·8	2·28	554
41·8	41·8	5100	16·5	1·21	549
43·3	43·3	8100	13·5	0·57	600

TABLE III.

Variation of methane pressure.

$\lambda = 3650$ A. $[Cl_2] = 45$ mm. $[HCl] = [CH_3Cl] = 5$ mm. $I_{\text{abs.}} = 7·8 \times 10^{13}$ quanta/sec.

$[CH_4]$, mm. ...	21·2	44·0	44·8	194·6	294·7	394·3
t, secs.	80	80	60	50	50	50
$\gamma \times 10^{-3}$	1·47	2·38	2·63	3·39	3·34	3·30

TABLE IV.

Variation of chlorine pressure.

$[CH_4] = 45$ mm. $[HCl] = [CH_3Cl] = 5·0$ mm.

(*a*) $\lambda = 4060$ A.

$[Cl_2]$, mm.	46·4	98·5	193·5	294	345	398	395
$I_{\text{abs.}} \times 10^{-13}$ ...	0·175	0·167	0·177	0·159	0·159	0·180	0·175
t, secs.	600	450	300	250	250	250	250
$\gamma \times 10^{-3}$	5·72	10·0	20·5	31·4	23·2	17·0	19·1

(*b*) $\lambda = 3650$ A.

$[Cl_2]$, mm.	12·2	19·0	44·1	63·9	88·7
$I_{\text{abs.}} \times 10^{-13}$ ...	1·21	2·16	4·48	6·02	7·75
t, secs.	300	180	70	50	70
$\gamma \times 10^{-3}$	1·81	2·18	2·67	2·87	2·96

(*c*) $\lambda = 4060$ A.

$[Cl_2]$, mm.	44·5	92·8	183·5	275·5	371
$I_{\text{abs.}} \times 10^{-13}$ ...	0·277	0·53	0·96	1·30	2·73
t, secs.	800	300	300	400	300
$\gamma \times 10^{-3}$	3·52	6·41	8·1	6·7	4·9

TABLE V.

$[Cl_2] = [CH_4] = 45$ mm. $[HCl] = [CH_3Cl] = 5$ mm.

(*a*) *Variation of argon pressure.*

$\lambda = 3650$ A. $t = 70$ secs. $I_{\text{abs.}} = 7·9 \times 10^{13}$ quanta/sec.

[A], mm.	0	50	100	200	300	400	500
$\gamma \times 10^{-3}$	2·25	2·28	2·38	2·26	2·24	2·07	1·96

$\lambda = 4060$ A. $t = 1200$ secs. $I_{\text{abs.}} = 0·27 \times 10^{13}$ quanta/sec.

[A], mm.	0	50	100	200	300	400	500
$\gamma \times 10^{-3}$	3·77	3·82	4·04	3·76	3·65	3·64	3·69

TABLE V (*contd.*)

$[Cl_2] = [CH_4] = 45$ mm. $[HCl] = [CH_3Cl] = 5$ mm.

(*b*) *Variation of nitrogen pressure.*

$\lambda = 3650$ A. $I_{abs.} = 7{\cdot}9 \times 10^{13}$ quanta/sec.

$[N_2]$, mm.	0	50	100	200	300	**400**	**400**
t, secs.	35	35	35	50	70	**70**	**80**
$\gamma \times 10^{-3}$	2·96	2·24	1·81	1·47	1·34	**0·97**	**1·07**

$\lambda = 3650$ A. $I_{abs.} = 0{\cdot}147 \times 10^{13}$ quanta/sec.

$[N_2]$, mm.	0	50	200	400
t, secs.	450	600	750	1000
$\gamma \times 10^{-3}$	8·91	7·08	4·84	2·59

(*c*) *Variation of hydrogen chloride pressure.*

$\lambda = 3650$ A. $I_{abs.} = 7{\cdot}7 \times 10^{13}$ quanta/sec.

[HCl], mm. ...	5	65	115	215	315	**415**	**415**
t, secs.	35	35	35	35	35	**35**	**35**
$\gamma \times 10^{-3}$	2·36	2·49	1·85	1·96	1·70	**1·76**	**1·59**

$\lambda = 3650$ A. $I_{abs.} = 0{\cdot}135 \times 10^{13}$ quanta/sec.

[HCl], mm. ...	5	115	215	315	415
t, secs.	550	550	650	750	900
$\gamma \times 10^{-3}$	9·0	8·0	7·6	7·0	7·4

DISCUSSION.

The high quantum efficiency and the general reproducibility of rate results suggests that no occasional inhibitors were present in the system. The marked effect of oxygen (Table I) is to be noted; a quantum efficiency of 2200 in the absence of oxygen was reduced to 150 by 1 mm. and to 15 by 10 mm. of oxygen. Such quantum efficiencies can be expressed by the equation $\gamma = k/(a + [O_2])$, inverse proportionality to oxygen pressure being evident above 1 mm. ($Cl_2 = CH_4 = 45$ mm.). The corresponding pressure in the hydrogen–chlorine reaction is approximately 10 mm. ($Cl_2 = H_2 = 43$ mm.) (Norrish and Ritchie, *loc. cit.*), and in the chlorine–toluene reaction is approximately 300 mm. ($Cl_2 = 25$ mm., toluene pressure 10 mm.) (Ritchie and Winning, preceding paper).

Previous investigators have agreed, mainly by consideration of the heats of reaction of the possible chain processes, that CH_3 radicals and not hydrogen atoms are involved. If hydrogen atoms were concerned, then their removal by oxygen would be facilitated by hydrogen chloride, as in the hydrogen chloride reaction where postulated mechanisms are

$$H + O_2 + HCl = HO_2 + HCl; \qquad H + O_2 + HCl = H_2O + ClO$$

One experiment is included in Table I in which the presence of 210 mm. of hydrogen chloride with 6·0 mm. of oxygen showed no retarding effect at all; and therefore the large inhibiting effect of oxygen can only be explained by its attack on CH_3 radicals. Further investigation showed that hydrogen peroxide was absent from the above illuminated system, in contrast to hydrogen–chlorine–oxygen mixtures (Norrish, *Trans. Faraday Soc.*, 1931, **27**, 461), but formaldehyde was detected by means of chromotropic acid. The initiation and propagation of the chains may thus be represented by

$$Cl_2 + h\nu \longrightarrow Cl + Cl \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$Cl + CH_4 \longrightarrow HCl + CH_3 \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl \quad . \; . \; . \; . \; . \; . \quad (3)$$

Of first importance in the elucidation of the chain-ending process is the intensity index *n* in the relationship $-d[Cl_2]/dt \propto I_{abs.}^{\,n}$. From Table II*a*, it is evident that at the higher intensities, over the range $I_{abs.}$ $7{\cdot}9 \times 10^{13}$ to $0{\cdot}76 \times 10^{13}$ the index is approximately unity, but at lower intensities the quantum efficiency rises, corresponding to a decreased value of *n*. Table II*a* refers to results obtained with the A.C. mercury-vapour lamp used generally throughout, when the illumination was thus intermittent (50 cycles per sec.), and accordingly this series of experiments was repeated with a direct-current mercury lamp, results being quoted in Table II*b*. Although absolute values appear to be some 30% less for the continuous light source, the index *n*, approximately unity at high intensities, becomes less than unity at low $I_{abs.}$, the change becoming appreciable again at an $I_{\text{abs.}}$ value of approximately 1×10^{13} quanta per sec. Values of n as obtained from the smoothed graphs of $I_{\text{abs.}}$ against γ for both series are given below.

	$I_{\text{abs.}} \times 10^{-13}$	8·0	4·0	1·0	0·5	0·4	0·3	0·2
Intermittent current	$\gamma \times 10^{-3}$	2·25	2·30	2·45	2·80	3·0	3·4	4·1
	n	—	0·97	0·95	0·81	0·69	0·56	0·54
Continuous current	$\gamma \times 10^{-3}$	1·50	1·55	1·70	2·05	2·2	2·5	3·0
	n	—	0·95	0·91	0·75	0·68	0·56	0·55

It has been urged by Bodenstein (*Ber.*, 1942, **75**, *A*, 119; *Z. physikal. Chem.*, 1941, *B*, **48**, 254) that the method of light intensity reduction, by means of filters and blue glass plates placed in the path of the light beam, is suspect and may lead to results of the above form if the beam is not monochromatic. The method was therefore applied to a reaction in which the rate is undoubtedly directly proportional to $I_{\text{abs.}}$, when the absorbing chlorine was at the same pressure, and the experimental arrangements, filters, etc., were otherwise as before. The reaction selected as most convenient in the present instance was the hydrogen–chlorine–oxygen reaction, for which n is unity for $[Cl_2] = 45$, $[H_2] = 45$, $[O_2] = 10$ mm. (Norrish and Ritchie, *loc. cit.*). This reaction rate at the lower intensities here in question is very low and it was not practicable to reduce the intensity to less than one-twentieth of the normal maximum value (11·9 to $0·57 \times 10^{13}$). These results are given in Table II*c*; it will be observed from the relative values of quantum efficiency that linearity exists between rate and $I_{\text{abs.}}$ over the range. In Table II*a*, $I_{\text{abs.}}$ for $\lambda = 3650$ A. is reduced similarly to approximately one-twentieth of the same normal maximum, but the decrease in n is already appreciable (from 0·97 to 0·69); and the results for $\lambda = 4060$ A. fall satisfactorily in the expected positions. For these reasons it is believed that the index variation observed is an essential feature of the reaction mechanism.

The occurrence of index values approaching 0·5, confirming the earlier work of Tamura (*loc. cit.*), indicates chain-ending by recombination of chain carriers. Possible reactions are:

$$CH_3 + CH_3 \longrightarrow C_2H_6 \quad \ldots\ldots\ldots \quad (4a)$$

$$CH_3 + Cl \longrightarrow CH_3Cl \quad \ldots\ldots\ldots \quad (4b)$$

$$Cl + Cl + M \longrightarrow Cl_2 + M \quad \ldots\ldots\ldots \quad (4c)$$

Apart from the fact that no chlorinated ethane was observed by Coehn and Cordes (*loc. cit.*), none of these possibilities predicts the experimental result that at high intensities the quantum efficiency becomes independent of $I_{\text{abs.}}$. Under certain conditions, the occurrence of an index value of unity may be explained by surface removal of chain carriers, for example, by diffusion to the vessel surface. If, however, chain carriers are removed by two possible processes, the rate of one being proportional to the square of the carrier concentration and that of the other proportional to the concentration, as would be the case for diffusion, then at high $I_{\text{abs.}}$ the former will be favoured, and the rate, proportional to $I_{\text{abs.}}$ at low intensities, will become proportional to $I_{\text{abs.}}^{\frac{1}{2}}$ at high intensity. The converse is true for the present experiments.

If the rate S of surface removal of chain carriers is determined mainly by convection, and surface removal is predominant, S will increase as $I_{\text{abs.}}$ is increased, by reason of the increased rate and heat of the reaction and the increased convection. The quantum efficiency would then show a constantly decreasing value ($\propto 1/S$), again in contrast to the present results.

The general reproducibility of experiment indicates that extraneous inhibitors, if present, must be in approximately constant amounts, the kinetics being then comparable to the diffusion surface action above discussed if the inhibiting action is of first order with respect to the chain carrier; if it is of second order, the change of index n to unity at high $I_{\text{abs.}}$ again cannot be explained. It would then appear that the chain-ending species must be produced by and be dependent on the light action; and the only possibility then seems to be the Cl_3 complex. To the previous initiation and chain processes we therefore add

$$Cl + Cl_2 + M \longrightarrow Cl_3 + M \quad \ldots\ldots\ldots \quad (4)$$

$$Cl_3 + M \longrightarrow Cl_2 + Cl + M \quad \ldots\ldots \quad (5)$$

$$Cl_3 + Cl_3 \longrightarrow 3Cl_2 \quad \ldots\ldots\ldots \quad (6)$$

By the stationary-state method, the quantum efficiency of chlorine removal is then

$$\gamma_{Cl_2} = \frac{2k_2[CH_4]}{k_4[Cl_2][M]}\left[1 + \frac{k_5[M]}{2k_6}\sqrt{\frac{1}{I_{\text{abs.}}}}\right]$$

When $I_{\text{abs.}}$ is the only variable, this reduces to $\gamma_{Cl_2} = a(1 + b/\sqrt{I_{\text{abs.}}})$, the quantum efficiency being thus independent of $I_{\text{abs.}}$ at high intensities, but becoming inversely proportional to $\sqrt{I_{\text{abs.}}}$ at low intensities, in agreement with experiment.

All reactant and resultant molecules must be considered as playing the part of M molecules, and $k_4[Cl_2][M]$ is therefore composite and must be written as

$$[Cl_2](k_4^{Cl_2}[Cl_2] + k_4^{CH_4}[CH_4] + k_4^{HCl}[HCl] + k_4^{CH_3Cl}[CH_3Cl] + k_4^{M}[M])$$

Similarly, $k_5[M]$ is to be replaced by $k_5^{Cl_2}[Cl_2] + \ldots\ldots\ldots$, where $k_4^{Cl_2}/k_5^{Cl_2} = k_4^{CH_4}/k_5^{CH_4}$, etc. For conditions in which the $I_{\text{abs.}}$ term is inappreciable, *i.e.*, at high intensities, the addition of, say, argon or nitrogen will decrease the quantum efficiency without altering the intensity relationship, but if the coefficient k_5 is large, the $I_{\text{abs.}}$ term will increase and the rate of reaction will tend to become proportional to $\sqrt{I_{\text{abs.}}}$. A partial approach to this state appears to exist in the index values for high hydrogen chloride pressures, but not for nitrogen or argon (see Table VI, based on results of Table V).

TABLE VI.

Gas pressure, mm.	0	100	200	300	400
n (HCl)	0·73	0·67	0·65	0·65	0·65
n (A)	0·76	0·76	0·76	0·76	0·75
n (N_2)	0·72	0·71	0·71	0·72	0·73

Since CH_4 must also be considered in this connection, the quantum efficiency will only be proportional to methane pressure at low pressures, and at high pressures will tend to become independent of $[CH_4]$, in agreement with experiment. Increase of chlorine pressure ought always to produce a decreased quantum efficiency, but experimentally such an effect is not observed until $[Cl_2]$ is greater than 100 mm. at high $I_{\text{abs.}}$, 200 mm. at intermediate values of $I_{\text{abs.}}$, and 300 mm. at low $I_{\text{abs.}}$ (Table IV).

It is then possible that diffusion of chain carriers to the vessel surface is of importance. The initial addition of argon does produce a small increase in γ (Table V*a*) at low $I_{\text{abs.}}$, as would be expected by decreased diffusion. If the diffusion reaction is

$$CH_3 \longrightarrow \text{surface} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (S_1)$$

then at high $I_{\text{abs.}}$, when the $I_{\text{abs.}}$ term is negligible, the quantum efficiency becomes

$$\gamma = \frac{2k_2[CH_4](k_3[Cl_2] + S_1)}{k_2[CH_4]S_1 + k_2[Cl_2][M](k_3[Cl_2] + S_1)}$$

If the diffusion reactions are :

$$Cl \longrightarrow \text{surface} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (S_2)$$

$$Cl_3 \longrightarrow \text{surface} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (S_3)$$

at high $I_{\text{abs.}}$, when the $I_{\text{abs.}}$ term is negligible,

$$\gamma = 2k_2[CH_4]/\{k_4[Cl_2][M](1 + S_2/k_4[Cl_2][M])\}$$

When the $I_{\text{abs.}}$ term is included, the expressions are complex and contain terms in S_1 and S_3, respectively. Further experiment is necessary, particularly on the variation of methane pressure at low intensities, to confirm or distinguish between these possibilities. In both cases, increase of chlorine pressure will initially increase the quantum efficiency by decreasing the rates of diffusion. Other chain endings are possible, *e.g.*, the reaction between CH_3 radicals and Cl_3 complexes.

The above results, however, show a decided similarity to the corresponding hydrogen–chlorine photoreaction (Ritchie and Taylor, *loc. cit.*), and by neglect of the supposed diffusion or other factor, relative values of certain coefficients may be obtained for comparison.

The following table shows that the variation of γ with $I_{\text{abs.}}$ can be fairly satisfactorily represented by $\gamma_{\text{calc.}} = a(1 + b\sqrt{I_{\text{abs.}}})$:

$$a = 2{\cdot}0 \times 10^3;\ b = 1{\cdot}20 \times 10^6.$$

$$[Cl_2] = [CH_4] = 45 \text{ mm.} \quad [HCl] = [CH_3Cl] = 5 \text{ mm.}$$

$I_{\text{abs.}} \times 10^{-12}$	79·0	44·8	7·57	4·02	2·77	1·74
$\gamma_{\text{exp.}} \times 10^{-3}$	2·20	2·37	2·54	2·73	3·52	4·56
$\gamma_{\text{calc.}} \times 10^{-3}$	2·27	2·36	2·88	3·00	3·44	3·82
$\gamma_{\text{calc.}}/\gamma_{\text{exp.}}$	1·04	1·00	1·13	1·10	0·98	0·84

In the hydrogen–chlorine reaction, with $[H_2] = [Cl_2] = 43$ mm., $[HCl] = 15$ mm., the corresponding value of a is markedly different (11,200) as would be expected from the substitution of methane by hydrogen in reaction (2), but the value of b is of the same order, *viz.*, $0{\cdot}91 \times 10^6$. Any change in b $(= k_5[M]/\sqrt{2k_6})$ is determined essentially by M $(= Cl_2 + k_M'M')$, since the same reactions are involved in the two cases, at the same temperature. Methane and methyl chloride must be expected to have greater efficiencies than hydrogen and hydrogen chloride, in such reactions, because of their greater molecular complexity; the slightly greater value of b in the methane chlorination is in agreement with such a view. The velocity coefficient k_2 of the reaction between chlorine atoms and methane (from $a = 2k_2[CH_4]/k_4[M][Cl_2]$) is thus approximately $(11{\cdot}2/2{\cdot}0) \times (1{\cdot}20/0{\cdot}91) = 7{\cdot}5$ times less than the corresponding Cl–H_2 reaction at 25°. Taking this collision efficiency as $3{\cdot}5 \times 10^{-5}$ (Rodebush and Klingelhœfer, *J. Amer. Chem. Soc.*, 1933, **55**, 130), we find the collision efficiency of reaction (2) to be approximately $0{\cdot}5 \times 10^{-5}$.

If $k_4^{\mathrm{CH_4}}$ is taken as unity, and the $I_{\mathrm{abs.}}$ term of the general expression assumed to be small and constant, the variation of γ with CH_4 pressure may be represented by

$$\gamma_{\mathrm{calc.}} = \frac{212 \times 10^3[CH_4]}{[Cl_2](k_4^{\mathrm{Cl_2}}[Cl_2] + k_4^{\mathrm{HCl}}[HCl] + k_4^{\mathrm{CH_3Cl}}[CH_3Cl] + [CH_4])}$$

when at $[Cl_2] = 45$ mm., $[HCl] = [CH_3Cl] = 5$ mm., the summation $k_4^{\mathrm{Cl_2}}[Cl_2] + k_4^{\mathrm{HCl}}[HCl] + k_4^{\mathrm{CH_3Cl}}[CH_3Cl]$ is 50. This is shown in the following table.

$[Cl_2] = 45$ mm. $[HCl] = [CH_3Cl] = 5$ mm.

$[CH_4]$, mm.	$\gamma_{\mathrm{exp.}}$ $\times 10^{-3}$.	$\gamma_{\mathrm{calc.}}$ $\times 10^{-3}$.	$\gamma_{\mathrm{exp.}}/\gamma_{\mathrm{calc.}}$	$[CH_4]$, mm.	$\gamma_{\mathrm{exp.}}$ $\times 10^{-3}$	$\gamma_{\mathrm{calc.}}$ $\times 10^{-3}$.	$\gamma_{\mathrm{exp.}}/\gamma_{\mathrm{calc.}}$
21·2	1·47	1·42	1·04	100	3·10	3·17	0·98
44·0	2·38	2·23	1·07	194·6	3·39	3·78	0·90

The variation of γ with argon pressure (Table V*a*) shows no change in the intensity index (Table VI), but at low intensity a small initial increase is to be observed with increasing argon content, an increase already ascribed to decreased diffusion. At high $I_{\mathrm{abs.}}$, in agreement with expectation, the retarding effect is more pronounced, but in the absence of a recognised diffusion process, only a very approximate value of the k_4 argon coefficient can be obtained. At the higher pressures, when diffusion will be less, the results indicate a k_4^{A} coefficient of approximately 0·1 $(k_4^{\mathrm{CH_4}} = 1{\cdot}0)$. This will be a minimum value. In the nitrogen series, diffusion will still be in operation, but the coefficient $k_4^{\mathrm{N_2}}$ is obviously appreciable and may be derived with greater accuracy from the high-intensity results of Table V*b*. From the results at 200 and 400 mm. pressure, $k_4^{\mathrm{N_2}}$ is calculated as 0·37 $(k_4^{\mathrm{CH_4}} = 1{\cdot}0)$. Similar calculations applied to the hydrogen chloride series (Table V*c*) indicate a k_4^{HCl} of approximately 0·2. With the exception of HCl, these coefficients are relatively in the same order $(k^{\mathrm{A}} < k^{\mathrm{N_2}} < k^{\mathrm{CH_4}})$ as already determined for other triple collision processes (Ritchie, *J.*, 1937, 863; Rabinowitch and Wood, *J. Chem. Physics*, 1936, **4**, 497).

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