397. *The Photochemical Union of Hydrogen and Chlorine. Part VI. The Mechanism of the Reaction at Low Hydrogen Pressures in Absence of Oxygen.*

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Experimental.

In Part V (preceding paper), it was stated that, at constant incident intensity, the rate of reaction under our conditions of experiment rose to a maximum as p_{Cl_2} increased, and then fell off. In the earlier work, the maximum was found at either 13 or 45·7 mm., whilst in a large number of experiments, carried out under a variety of conditions, the "slope" (see Part V) at 1·7 mm. was always less than that at 13 mm. In the more recent work, the maximum rate was found at 82·6 mm. of chlorine in one case, whilst in other, less complete sets of measurements, it lay at 45·7 mm. Moreover, in agreement with the observed relation between absorbed intensity and n, it moved towards high chlorine pressures as the incident intensity decreased [*e.g.*, Part V, Table IV, (*a*) and (*c*): Expts. IV, h, i; VI, a, g].

This retarding effect of chlorine is shown to its full extent when, at constant incident intensity, quantum efficiencies are compared. The majority of the later and many of the earlier experiments can be treated in this way, the necessary data (absolute intensity of light beam, spectral energy distribution therein, extinction coefficients of chlorine, slopes, volume of reaction zone) being available. Table I contains these γ values, referred to hydrogen and calculated for a hydrogen pressure of 0·1 mm., for all cases where three or more chlorine pressures can be compared with one another. Expts. 56 and 57 are included for a particular reason. Where pairs of values are quoted, the second refers to the lower of two absorbed intensities, the ratio of which is given in the last column.

In every case, γ rises as intensity decreases, and to a greater degree the higher the chlorine pressure. The absolute rates of quantum absorption for the latter experiments are given in Table IV of Part V. In the mercury-arc experiments, the absorbed intensities were higher in the earlier than in the later work. In qualitative agreement with this difference, the γ values are lower in the earlier experiments. To this statement there is one marked exception. In Expts. 42—54 and 56—57 (two different series), a quartz-mercury lamp without any filter was used, and the rates of quantum absorption were consequently unusually high. In spite of this, the values of γ at low pressures of chlorine were the highest observed. The figures in parentheses

Table I.

Values of quantum efficiency at p_{H_2} = 0·1 *mm. and at different chlorine pressures.*

	Chlorine pressure, mm.								
Expts.	0·012.	0·11.	1·7.	13·0	45·7.	82·6.	166.	450.	
24—26 (4)	—	—	11·1	12·2	6·9	—	—	—	
34—39, 41 (7)	—	—	13·2	18·2	22·4	—	4·8	—	4·35
	—	—	13·7	21·3	30·1	—	7·4	—	
42, 43, 52 (8) ...	270	—	147	55	—	—	—	—	
56, 57 (10)	—	—	—	50	14	—	—	—	
58—62 (11) ...	—	(1·00)	(1·01)	(1·09)	(0·77)	—	(0·17)	—	
V, a, b, c	—	—	—	—	35·0	—	6·16	0·80	2·36
	—	—	—	—	42·3	—	11·6	1·49	
VI, a, d, e, f, g	—	—	—	46·3	42·1	32·6	9·75	1·25	4·60
	—	—	—	61·5	61·9	59·5	26·5	3·76	
IX, a, e, g	—	—	—	—	38·4	22·2	7·02	—	5·65
	—	—	—	—	52·1	32·9	16·8	—	
IX, c, i, j	—	—	—	—	—	33·6	12·8	0·94	5·65
	—	—	—	—	—	42·2	25·2	1·90	
X, a, f, k	—	—	—	—	—	3·18	0·36	0·056	5·65
	—	—	—	—	—	7·75	1·85	0·27	
X, b, g, m	—	—	—	—	—	7·17	2·08	0·30	5·65
	—	—	—	—	—	13·7	6·1	0·93	

Note.—The pairs of values enclosed within dotted frames were obtained by insolation with the same intensity in different experiments.

for Expts. 58—62 (glass apparatus; tungsten-filament lamp; no filter) are relative values only, no absolute intensity measurements being available.

With the exception of the remarkable group of results given by Expts. 42—57, the maximum γ value is seen to fall sometimes at 13·0, sometimes at 45·7 mm. of chlorine, and there are indications that, the lower the intensity, the higher would be this optimum pressure. At higher chlorine pressures, γ falls off ever more and more steeply.

Table II contains the " order " according to which the chlorine takes part in the reaction at constant incident intensity when p_{Cl_2} increases from 82·6 to 166, and from 166 to 450 mm., effects due to the changed absorption of light being eliminated by using the equation $\gamma_{p_1}/\gamma_{p_2} = (p_2/p_1)^m$. The first value of m is derived from the experiments at the higher intensity.

TABLE II.

82·6—166 mm.		166—450 mm.	
Expts.	m.	Expts.	m.
VI, d, g	1·73, 1·16	V, a, b	2·05, 2·06
IX, a, g	1·65, 0·96	VI, f, g	2·06, 1·96
IX, c, i	1·38, (0·75)	IX, i, j	(2·62), (2·59)
X, f, k	(3·12), 2·05	X, a, f	1·87, 1·93
X, g, m	1·77, 1·16	X, b, g	1·94, 1·89
		X, c, h	2·08, 2·00
		X, d, i	1·94, 1·66

Some discrepant figures have been enclosed in parentheses. We cannot account for them, but it may be remarked that attention was drawn in Part V to the abnormal results of IX, i, j, and that the results obtained at the higher intensities in X, a, k showed an unusual lack of reproducibility. Apart from them, it is clear that γ varies in proportion to the inverse square power of p_{Cl_2} as this increases from 166 to 450 mm., whilst in the interval 82·6—166 mm., the kinetic " order " of the chlorine lies between — 1 and — 2, the latter figure being approached as the intensity increases.

TABLE III.

p_{Cl_2} = 0·012 mm.			p_{Cl_2} = 0·11 mm.			p_{Cl_2} = 1·7 mm.		
Series 8.			Series 11.			Series 8.		
Expt.	p_{HCl}.	Slope.	Expt.	p_{HCl}.	Slope.	Expt.	p_{HCl}.	Slope.
52	0·0	0·22	58	0·0	0·21	43	0·28	15·1
46	6·9	1·6	62, a	3·36	0·34	45 b	6·7	11·8
51	8·6	1·4	62, b	4·74	0·50	48, 50	46·2	6·6—12·2 *

p_{Cl_2} = 1·7 mm.

Series 3. Normal incident intensity.			Series 3. Much reduced incident intensity.			Series 4.		
13	0·46	2·2—3·7 (mean 2·8)	17	1·3	0·022	25	0·26	0·60
20	10·8	2·2	19	10·4	0·032	29	10·9	1·7
22	11·0	2·9						

p_{Cl_2} = 13·0 mm.

Series 3. Normal incident intensity.			Series 3. Much reduced incident intensity.			Series 4.		
12	0·12	11·2	16	1·2	0·16	24	0·0	3·45
23	11·3	12·6	18	10·0	0·20	28	10·7	5·4
Series 7.			Series 8.			Series 13.†		
36	0·80	5·2	42	0·0	26	68	0·80	5
40	10·7	6·34	47	45·4	14	73	318	0·38

p_{Cl_2} = 45·7 mm.

Series 4.			Series 7.		
Expt.	p_{HCl}.	Slope.	Expt.	p_{HCl}.	Slope.
26	0·44	3·4	34, 35	0—0·4	10·4—11·8
27	10·5	5·5	38	10·0	10·7

* Very irregular results. † Traces of oxygen present.

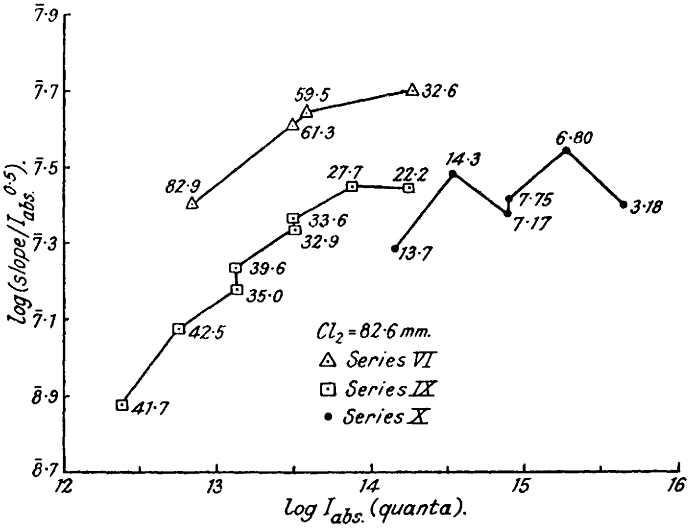
The only other experimental data to be considered concern the effect of added hydrogen chloride. A number of such experiments were made during the earlier work, and the results are collected in Table III (pressures of hydrogen chloride in mm.). It is plain that, at the two lowest chlorine pressures used, a few mm. of added hydrogen chloride accelerate the reaction. The effect of the addition of 10—11 mm. on the reaction rate at higher chlorine pressures is, at first sight, not very clear, but inspection shows two factors to be involved, *viz.*, (i) the rate of reaction in absence of added hydrogen chloride, and (ii) the chlorine pressure. Addition of hydrogen chloride tends to accelerate a slow reaction, to have less effect as this rate becomes greater, and to retard a rapid reaction. Quite generally, under the same conditions of illumination, the slopes found in the different series increased in the order $4 < 7 < 3 < 8$, being very high in the last case (Expts. 42, 43, 52 of Table I). The relative effects of adding 10 cm. of hydrogen chloride at different chlorine pressures are all in accord with this progression; *e.g.*, at $p_{\mathrm{Cl}_2} = 1{\cdot}7$ mm., there is a three-fold acceleration in series 4, no appreciable effect in 3, and actually a retardation in 8 when 6·7 cm. are added. The evidence at the other chlorine pressures is similar. Differences in slope due to differences in incident intensity are related in the same way to the effect of added hydrogen chloride, as is seen in Series 3, experiments at 1·7 and 13 mm. of chlorine. The effect of p_{Cl_2}, when the experiments at 0·012 and 0·11 mm. are taken into account, can also not be doubted, notwithstanding the relative results at 1·7 and 13 mm. of chlorine in Series 3 (normal intensities) and at 13 and 45·7 mm. in Series 4. The lower p_{Cl_2}, the greater the accelerating effect of a few mm. of added hydrogen chloride.

We have very few results at higher hydrogen chloride pressures. In Series 8, 46 mm. of the gas reduce the velocities at p_{Cl_2} values of 1·7 and 13 mm. In view of what has been said, it is by no means certain that a similar retardation would have taken place, for example, during experiments in Series 4. The very considerable effect at 13 mm. of chlorine caused by adding 318 mm. of hydrogen chloride is accompanied by a reduction of the intensity exponent from its normal figure of 0·9 to 0·72 (Part V, Table II, Expt. 73).

DISCUSSION.

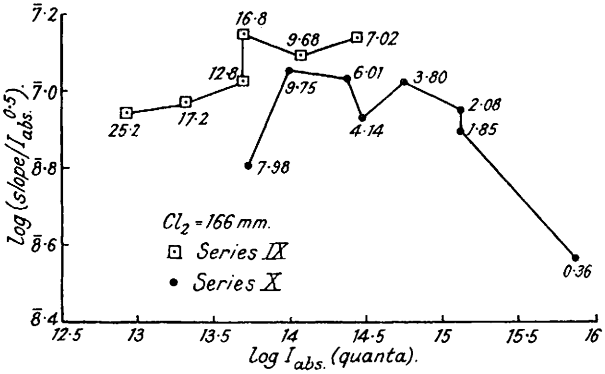
It was shown in Part V that the exponent *n*, governing the velocity ratio found at two different intensities, decreases as the absolute values of the latter increase, starting at above 0·5 at low intensities and, in the case of experiments with 166 and 450 mm. of chlorine, falling well below this figure at the higher intensities. It is important to determine whether, over a finite intensity range, *n* remains constant at 0·5 before falling further. If that be the case, the graph of log (slope/$I_{\mathrm{abs.}}^{0\cdot5}$) against log $I_{\mathrm{abs.}}$ should run parallel to the axis of the latter in such an intensity region. Such curves for pressures of 82·6, 166, and 450 mm. of chlorine are reproduced in Figs. 1—3. The figures adjacent to the experimental points are

FIG. 1.



the γ values as given in Table I. Although the experimental errors are rendered very obvious, there can be no doubt that such an intensity region of constant *n* does exist in each case, and that it commences at a lower absorbed intensity with a mercury than with a tungsten lamp. In the case of the experiments at 82·6 mm., there is no subsequent falling off in the curve at higher intensities. Similar graphs were made for this pressure of log (slope/$I_{\text{abs.}}^{0\cdot3}$) and of log (slope/$I_{\text{abs.}}^{0\cdot7}$) against log $I_{\text{abs.}}$; in neither case was there any

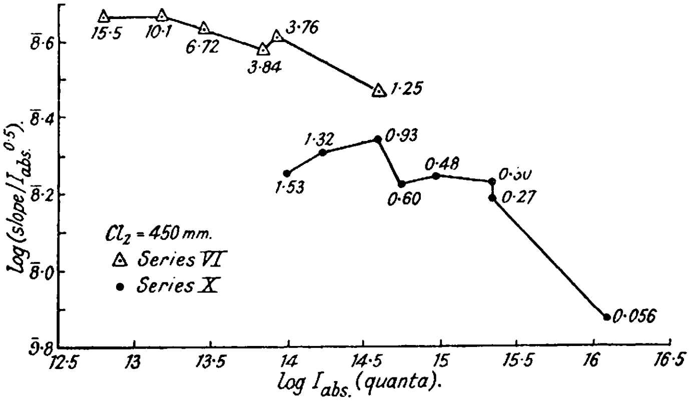
FIG. 2.



tendency towards a portion of the curve running parallel to the intensity axis. In accordance with familiar arguments, we therefore conclude that, when both intensity and also chlorine pressure are sufficiently high, the reaction chains end in the gas phase by the combination of two carrier units, and that, at still higher intensities, a further factor enters which, in some way, masks this process.

In view of the known greater efficiency (a ratio of 10^2—10^3) of H–Cl_2 as compared with Cl–H_2 collisions, and of the great preponderance of chlorine over hydrogen in our experiments, there can be no question of hydrogen atoms being involved, and the most obvious suggestion is that chains are ended by a triple collision of the Cl + Cl + M type. This conclusion is, however, forbidden by the fact that, at total pressures of 13—14 mm. (Part V, Table II), the intensity exponent is consistently as low as 0·9, indicating that an important fraction of the chains is broken in the gas phase by the process under discussion, whatever its nature. At such pressures, triple collisions are exceedingly rare events, and a termolecular mechanism could not possibly play an appreciable part in the terminating chains. Some process which does not involve a triple collision is required.

FIG. 3.



In Part IV (J., 1936, 241), when discussing the fact that, in oxygen-free gases at low total pressures, the value of γ was 30—40% less for ultra-violet than for visible light, we suggested that the cause was the interaction with chlorine molecules of chlorine atoms of high translatory energy freshly formed by photo-dissociation, the result being the production of Cl_3 radicals at a concentration higher than would correspond to the Cl–Cl_2–Cl_3 equilibrium under the conditions of illumination. These radicals would react less readily with hydrogen molecules than would chlorine atoms, and would also probably be adsorbed more easily on the walls of the reaction cell; hence the reaction chains would become shorter and γ diminish. The assumption that such Cl_3 radicals, no longer selectively formed by ultra-violet light, but present in equilibrium concentration, play an essential part in the experiments now under discussion, has enabled us to explain satisfactorily, not only the intensity law found in our experiments, but also the remarkable retarding effect of chlorine. In discussing our results, complex because such wide ranges of chlorine pressure and intensity have been covered, it will be simplest first to deal with those experiments with 82·6 mm. of chlorine in which the $I^{0.5}$ relation was found to hold closely over a considerable range of intensity. Those chosen for review will be X, k, l, m [Fig. 1 and Part V, Table IV (*b*)].

Experiments obeying the $I^{0.5}$ *relation.* The proposed mechanism comprises the following steps:

$$\begin{array}{llll} (1) & Cl_2 + h\nu \longrightarrow 2Cl & (4) & Cl + Cl_2 \longrightarrow Cl_3 \\ (2) & Cl + H_2 \longrightarrow HCl + H & (5) & Cl_3 \longrightarrow Cl + Cl_2 \\ (3) & H + Cl_2 \longrightarrow HCl + Cl & (6) & 2Cl_3 \longrightarrow 3Cl_2 \end{array}$$

It is further assumed that the equilibrium expressed by

$$K = [Cl_3]/[Cl][Cl_2] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

is maintained, or practically so, during the course of the reaction, which signifies that (4) and (5) are relatively so rapid that, when the stationary state has been set up, neither (1) nor (6) can appreciably disturb equilibrium (7). Step (3), for reasons already given, will follow very closely on (2), so that neither [Cl] nor [H] will be thereby affected. Both (4) and (5) can be regarded, if wished, as involving another reaction partner M. According, however, to Rollefson and Eyring (*J. Amer. Chem. Soc.*, 1932, **54**, 170), the quasi-molecule Cl_3 " will have a very long life, as compared with the duration of an ordinary collision." (6), of course, will not require the intervention of a third body in order to produce stable molecules of chlorine. Any reaction such as $Cl_3 + H_2 \longrightarrow Cl_2 + HCl + H$ is neglected. According to Kimball and Eyring (*ibid.*, p. 3876), the efficiency of this collision is 10^{-3}—10^{-4} times that of Cl–H_2 collisions, whilst Rollefson (*ibid.*, 1934, **56**, 579) gives reasons for preferring a ratio of 10^{-1}—10^{-2}. In any case, its introduction would make the velocity equation more complex, whilst altering the nature of the results very slightly.

Working through the above equations in the usual manner due to Bodenstein, we arrive at the result

$$\gamma_{(H_2)} = k_2\,[H_2]/K_7[Cl_2](k_6\,.\,I_{abs.})^{0.5} \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

an expression which reproduces the required first order for hydrogen and the value of 0·5 for n, and, in addition, is of the inverse first order for chlorine. From the γ data (quoted on Fig. 1—in part in Table I), the rates of quantum absorption [Fig. 1; Part V, Table IV (*b*)] and the values of k_2 and k_6, K_7 can clearly be found. In all calculations which follow, a temperature of 18° is assumed, and the units of 1 c.c. and 1 second employed. The volume of the reaction cell was 490 c.c., and the quanta absorbed per second are therefore the figures quoted in the table divided by $10^{2.69}$. The coefficients k_2, k_6, etc., have been worked out by the standard methods for 1 mm. pressure of each reactant, and pressures in mm. are introduced into equation (8) instead of concentrations. The value of K_7 which results is therefore K_p of dimensions mm.$^{-1}$. The atomic and molecular diameters (in A.) assumed are: H_2 2·46, Cl_2 4·96, Cl 3·36, Cl_3 6·66. In agreement with Rodebush and Klingelhoefer (*ibid.*, 1933, **55**, 130), we have taken the efficiency of Cl–H_2 collisions as 3.5×10^{-5} ($E = 5.94$ kg.-cals.), and that of Cl_3–Cl_3 collisions as unity. As always, γ values refer to molecules of hydrogen or chlorine at 0·1 mm. of hydrogen, whilst i and ii, here and later, indicate experiments carried out at high and at low intensities respectively.

TABLE IV.

$p_{H_2} = 0{\cdot}1$; $p_{Cl_2} = 82{\cdot}6$; $k_2 = 10^{19{\cdot}46}$; $k_6 = 10^{23{\cdot}72}$.

Expt.	X, k, i	X, k, ii	X, l, i	X, l, ii	X, m, i	X, m, ii
log $I_{abs.}$	12·96	12·21	12·59	11·83	12·21	11·46
γ	3·18	7·75	6·80	14·3	7·17	13·7
log K	− 2·30	− 2·31	− 2·44	− 2·39	− 2·28	− 2·18

The mean value of K_p is $10^{-2{\cdot}31}$ or 0·00491 mm.$^{-1}$, whereas the value calculated from the data given by Rollefson and Eyring as the most probable is 0·78 mm.$^{-1}$, *i.e.*, 160 times as high. Their figure depends on the assumptions that, for reaction (4), $-\Delta H$ and ΔS are 4·1 kg.-cals. and − 6 respectively. Using the same figure for the entropy change, we find that our value of K corresponds to $-\Delta H = 2{\cdot}5$ kg.-cals. : K is of course equal to k_4/k_5. The collision number, for pressures of 1 mm., corresponding to k_4, worked out as before, is $10^{23{\cdot}49}$. The most probable value of E_4, according to Rollefson and Eyring, is 4·5 kg.-cals., and the maximum possible figure 8·6 kg.-cals. The minimum figure consistent with our explanation of the low-pressure wave-length effect is 5·0 kg.-cals. (Part IV; *loc. cit.*, p. 250). With this as a basis, the efficiency of Cl–Cl$_2$ collisions becomes $10^{-3{\cdot}75}$ or $1{\cdot}78 \times 10^{-4}$, and the values of k_4 and of k_5 are $10^{19{\cdot}74}$ and $10^{22{\cdot}05}$ respectively. The activation energy of (5) will be 7·5 kg.-cals., as compared with the 8·6 kg.-cals. of Rollefson and Eyring.

Using the data of X, k, ii, where the found value of K coincides with the mean value, and the values of k_4 and k_5 just obtained, we may finally compare the absolute rates (molecules transformed per c.c. per sec.) in the different steps, in order to see whether equilibrium (7) is likely to be maintained on our assumptions. We calculate that, per c.c. and per sec., $10^{16{\cdot}29}$ chlorine atoms and Cl$_3$ radicals are formed and disappear in virtue of the opposed reactions (4) and (5), $10^{12{\cdot}50}$ chlorine atoms are produced by (1) and disappear by (6) after conversion into Cl$_3$ radicals, and $10^{12{\cdot}89}$ chlorine atoms react with hydrogen in accordance with (2), and are immediately regenerated by (3). It is plain that neither (1) nor (6) will appreciably disturb equilibrium (7).

The assumption that chain termination is the result of (6) is not the only one which can be made. Thus, the reaction

$$Cl + Cl_3 \longrightarrow 2Cl_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

may be responsible, or (6) and (9) acting in conjunction. The value of k_9, calculated in the usual way, is $10^{23{\cdot}62}$, very near that of k_6. If (9) only is active, then the equation for γ is identical with (8), except that k_6 must be replaced by $k_9/K_7[Cl_2]$, whilst if both (6) and (9) are operative simultaneously, $k_6 + k_9/K_7[Cl_2]$ must be used. The results of X, k, ii, are then satisfied if K_7 becomes, respectively, $10^{-2{\cdot}62}$ and $10^{-2{\cdot}67}$ mm.$^{-1}$, values 2 and 2·3 times lower than the one deduced on the basis of reaction (6). Whilst, however, (6) gives an equation in which γ varies inversely as the first power of the chlorine concentration, the kinetic " order " for chlorine becomes − 0·5 if (9) only is employed, and varies between − 1 and − 0·5 if both reactions are considered. For this reason, we regard (6) as the only significant chain-ending process at the higher chlorine pressures, whilst thinking it quite possible that (9) may play an increasing part as p_{Cl_2} becomes less.

There are, formally, two methods by which our value for K_7 could be brought into line with that calculated by Rollefson and Eyring, *viz.*, by increasing k_2 160-fold, or by decreasing k_6 (or k_9) by the factor $10^{-4{\cdot}4}$. The accepted figure of $3{\cdot}5 \times 10^{-5}$ for the efficiency of Cl–H$_2$ collisions at ordinary temperatures is well established, and to change it to $5{\cdot}6 \times 10^{-3}$ would be inadmissible. A collision efficiency as low as 4×10^{-5} for (6) would be exceedingly unlikely. It is probable that a steric factor of the order of 10 is involved in Cl$_3$–Cl$_3$ collisions, and that our figure for k_6 should be correspondingly reduced, whilst if a higher factor were assumed for Cl–Cl$_3$ collisions, the relative unimportance of k_9 would receive a ready explanation. Such adjustments would not appreciably affect K, and the discrepancy between our deductions and the calculations of Rollefson and Eyring must remain.

The low n value of 0·9 at total pressures of 13 mm. was mentioned above as the reason for rejecting the step,

$$2Cl + M \longrightarrow Cl_2 + M \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

leading to the very simple expression

$$\gamma_{(H_2)} = k_2[H_2]/(k_{10} \cdot I_{abs.})^{0.5}\,[M]^{0.5} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

Applied to X, k, ii, this necessitates k_{10} (bimolecular collision—consideration of M omitted) having a value of $10^{22.93}$ in the units employed (molecules × c.c.$^{-1}$ × sec.$^{-1}$ × mm.$^{-2}$). On calculation as before, the collision number at 1 mm. pressure is $10^{23.26}$, which means that 27% of all such bimolecular Cl–Cl collisions would have to be effective to account for the experimental results, and this at a total pressure of little over 0·1 atm., where the proportion of triple collisions is of the order of 10^{-3}—10^{-4}.

Experiments at high chlorine pressures and intensities. Equation (8) demands that γ should be inversely proportional to the chlorine pressure. Table II shows that, at relatively low intensities, this relation is approximately fulfilled as p_{Cl_2} changes from 82·6 to 166 mm., whilst at high intensities, the retarding effect is relatively higher. But on passing from 166 to 450 mm., the inverse power of p_{Cl_2} rises to 2, and, at the same time, and the more so the higher the intensity, n drops below 0·5 [Part V, Table IV, (*c*) and (*d*)]. It will be remembered that the whole volume of the reaction vessel was not insolated, a cylindrical beam of light passing axially down the cell. This suggested that possibly both the phenomena mentioned were due to retarded diffusion of hydrogen from the adjacent dark space into the illuminated zone. Such a view cannot be maintained, however. The actual rates of consumption of hydrogen in these experiments are very low, and the average displacement per second of a hydrogen molecule, calculated by the usual approximate formula, is 1·33 cm. at 450 mm. of chlorine, and 2·19 cm. at 166 mm. We think, nevertheless, that diffusion effects cause the results referred to, not diffusion of hydrogen into the insolated zone from outside, but diffusion of chlorine atoms out of this zone into the rest of the reaction space.

In our treatment of the experiments at 82·6 mm. of chlorine, we assumed that, owing chiefly to convection, the concentration conditions were essentially uniform throughout the whole cell. When, however, we consider the experimental conditions during work at higher chlorine pressures, where γ values are usually much lower, we find that, not only is the sum of the quantities of heat developed by light absorption and by reaction often less than at 82·6 mm. of chlorine, but also, owing to the higher heat capacity of the gases, the resulting temperature rise, and therefore any convection effects, are very much smaller. Thus, rough calculations on the results of the experiments at five different pressures carried out in Series VI (see Table I) indicate that, at a given incident intensity, the relative temperature rises in the illuminated zone are approximately as follows:

450 mm.	166 mm.	82·6 mm.	45·7 mm.	13 mm.
1	8—9	30—35	40	45

This being so, we assume that at these higher pressures, the reaction very largely completes itself inside the light beam, rather than uniformly throughout the whole cell.* If it were to be confined entirely to this insolated zone, then equation (8) would be obeyed, γ being low in consequence of the high concentration of absorbed light. But whilst the data would then necessarily follow the $I^{0.5}$ relation, the experimental figures do not, lower intensity exponents being found.

We think that both the intensity and the enhanced chlorine effects can be explained on the assumption that the reaction under these conditions takes place partly in the light and partly in the dark zone; that in the latter case it is due to chlorine atoms passing out of the beam into the dark space, there finally to disappear, after conversion into Cl_3 radicals, in accordance with (6); and that this movement of chlorine atoms is due at the highest pressures essentially to diffusion, convection playing a subordinate part. Chlorine atoms, rather than Cl_3 radicals, are suggested, as calculations show that the latter, with their slow diffusion rate and short life, cannot be responsible for the effect. Chlorine

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* The unusually low value of n found in Expts. 129—131 (Part V, Table III) is due to this same localised action, a consequence of low rate of reaction, heat evolution, and convection.

atoms, on the other hand, diffuse nearly twice as quickly, and, more important, do not disappear as the result of mutual collision. In any case, as soon as chlorine atoms or Cl_3 radicals have escaped from the light beam where they are present in high concentration, their life immediately becomes considerably greater, and increases as they diffuse outwards.

The longer this life, the longer the chain initiated by a chlorine atom. The higher the proportion of chlorine atoms which escape from the insolated zone into the dark space, the higher therefore the average value of γ. This proportion will decrease as the intensity, and hence the rate of production of chlorine atoms, increases; it will, indeed, decrease ever more rapidly after a certain point, a consequence of the finite distance that the atoms must travel before they can escape into the light zone. The result will be that, although in any given small volume element, chains propagate at a rate proportional to p_{Cl} and terminate at a rate proportional to $p^2_{\mathrm{Cl}_3}$, corresponding to the $I^{0\cdot5}$ relation, yet at high intensities the fraction of such chains terminated inside the light zone will be greater than at low intensities, and the overall value of n will fall below 0·5. A similar state of affairs was discussed at the end of Part V in connection with the differences between the results given by the mercury and the tungsten lamp. This effect will enter earlier, the higher p_{Cl_2} and hence the slower diffusion. Numerous calculations on these lines, whilst showing that the proposed explanation can account semi-quantitatively for the abnormal intensity exponents observed, have not been successful in leading to an exact treatment of the results, which is not surprising in view of the simplifications necessary.

With regard to the extra inverse power of the chlorine concentration, we assume the volume of the effective reaction zone to be essentially governed by the rate of diffusion of chlorine atoms outward from the central beam. This rate will be inversely proportional to p_{Cl_2}. If it were a question of diffusion in three dimensions from a point source of chlorine atoms, the volume of the reaction zone would be proportional to the cube of the diffusion coefficient, and hence inversely proportional to $p^3_{\mathrm{Cl}_2}$. But diffusion along the axis of the cell will have no effect on the reaction volume. We are concerned with diffusion in two dimensions only. Consequently, the reaction volume will vary as $p^{-2}_{\mathrm{Cl}_2}$, and the effective absorbed intensity as $p^2_{\mathrm{Cl}_2}$. The square root of $I_{\mathrm{abs.}}$ appears in the denominator of (8), and hence indirectly the first power of p_{Cl_2}.

The relation between p_{Cl_2} and γ over the range 82·6—166 mm. as set out in Table II shows that, at the latter pressure, the diffusion effect under consideration is only partly operative even at the higher intensities. When p_{Cl_2} is raised to 450 mm., however, the inverse square power of the chlorine indicates that, at this pressure and at the high intensities employed, it is fully active. Series X still being considered (all calculations are referred to experiments in this series in view of the more uniform spatial distribution of the absorbed tungsten-filament radiation), Fig. 3 and Table IV (*d*) of Part V suggest that equation (8) should be applicable to Expt. X, d. If we substitute the experimental data for γ and for $I_{\mathrm{abs.}}$, using the value of $10^{-2\cdot31}$ for K, as deduced from the experiments at 82·6 mm. of chlorine, we obtain 66 c.c. for the effective reaction volume, corresponding to a uniform column of 1·8 cm. diameter, which is quite plausible. If now we calculate from this value, by multiplying by $(450/166)^2$, the effective volume of the reaction zone at 166 mm. under limiting diffusion conditions, we get 485 c.c., practically identical with the volume of the reaction vessel. It is, however, doubtful whether such conditions could be realised at 166 mm., owing to convection disturbances. That they are partly operative at higher intensities is shown by the values of the intensity exponent, apart from the data in Table II.

The results of experiments at higher intensities cannot be treated in this way, owing to the fact that the $I^{0\cdot5}$ relation is not obeyed, which makes it impossible to use equation (8).

Experiments at lower chlorine pressures. Effect of added hydrogen chloride. Up to 1·7 mm. of chlorine, n is practically unity, indicating that, oxygen being absent, the reaction is ended by adsorption and recombination of chain carriers on the walls. Hydrogen atoms will play a negligible part, even at the lowest value of p_{Cl_2} used (0·012 mm.). Moreover, on the basis of the figure of $10^{-2\cdot31}$ calculated above for $K = p_{\mathrm{Cl}_3}/p_{\mathrm{Cl}}p_{\mathrm{Cl}_2}$, the ratio $[\mathrm{Cl}_3]/[\mathrm{Cl}]$ will be very low, even if this equilibrium were completely established, for which the conditions are not favourable. It is natural, then, to assume that the essential chain-ending reaction will be

$$\mathrm{Cl} \xrightarrow{\text{wall}} \tfrac{1}{2}\mathrm{Cl}_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

the expression for the quantum yield becoming

$$\gamma_{(\mathrm{H}_2)} = 2k_2[\mathrm{H}_2]/k_{12} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

The hydrogen pressure being expressed in mm., and k_2 being as before, k_{12} has the dimensions photon × c.c.$^{-1}$ × sec.$^{-1}$ × mm.$^{-1}$, and is directly calculable from the experimental results. Combining with it the rate of quantum absorption, we can compute the stationary value of p_{Cl}, and hence, by the standard formula, the rate at which chlorine atoms strike the walls of the reaction vessel and the efficiency of these collisions. Bodenstein and Winter (*Sitzungsber. preuss. Akad. Wiss.*, 1936, 1), who did such calculations in connexion with the kinetics of the reaction in oxygen-free gases at atmospheric pressure, recently reported an " accommodation coefficient " as low as $10^{-3 \cdot 8}$ for the adsorption of chlorine atoms on the walls of the silver reaction vessel used.

TABLE V.

Expt. and series :	52 (8).	46 (8).	51 (8).	43 (8).	45b (8).	25 (4).	29 (4).
p_{Cl_2} (mm.)	0·012	0·012	0·012	1·7	1·7	1·7	1·7
p_{HCl} (mm.)	0·0	6·9	8·6	0·28	6·7	0·26	10·9
γ	270	1960	1720	147	115	11·1	31·4
log K_{12}	16·33	15·47	15·52	16·59	16·70	17·71	17·26
log p_{Cl} (mm.)	– 6·93	– 6·07	– 6·12	– 5·09	– 5·20	– 6·49	– 6·04
log Cl atoms adsorbed by walls *	9·45	9·45	9·45	11·55	11·55	11·27	11·27
log collisions of Cl atoms on walls *	13·35	14·21	14·16	15·19	15·08	13·79	14·24
log collision efficiency	– 3·90	– 4·76	– 4·71	– 3·64	– 3·53	– 2·52	– 2·97

* Per cm.^{2} per second.

In Table V are contained the results of a number of calculations of this kind, for reactions at 0·012 and 1·7 mm. of chlorine, both in the presence and in the absence of added hydrogen chloride. The collision efficiencies are all very low, in agreement with the results of Bodenstein and Winter, as also with earlier direct observations of Rodebush and Klingelhoefer (*loc. cit.*) and of Schwab and Friess (*Z. Elektrochem.*, 1933, **39**, 586). They, moreover, vary over a wide range, in correspondence with observations made by us throughout this work.

According to (13), γ should be independent of p_{Cl_2} in this region, except in so far as this factor may affect k_{12}. When p_{Cl_2} becomes so high that n falls below unity, as is the case at 13 mm. of chlorine, indicating that chains are being ended in the gas phase, a fall off in γ would be expected. Table I shows an example of a rapid decrease in γ as p_{Cl_2} increases from 0·012 to 13 mm., and a number of cases in which γ_{13} definitely exceeds $\gamma_{1 \cdot 7}$. Examination of these data, as also of a number of unquoted comparisons made early in the work between γ_{13} and $\gamma_{1 \cdot 7}$, shows plainly (*a*) that if the γ values in a series are generally high (low catalytic action of walls), an increase in p_{Cl_2} decreases γ, whilst if the walls readily adsorb chlorine atoms, γ tends to rise with increase in p_{Cl_2}; (*b*) that, in any given series of experiments, the higher the incident intensity the smaller is the ratio $\gamma_{13} : \gamma_{1 \cdot 7}$.

We interpret these results as follows. An increase in p_{Cl_2} will reduce the extent of adsorption of chlorine atoms on walls which otherwise would readily catalyse their recombination. If, however, the " accommodation coefficient " of chlorine atoms is already abnormally low, such an effect of increased p_{Cl_2} will be imperceptible. On the other hand, the equilibrium ratio $p_{\mathrm{Cl}_3}/p_{\mathrm{Cl}}$ is 140 times higher at 1·7 than at 0·012 mm. of chlorine, and the chances that this equilibrium will be approached are much greater. As was assumed in Part IV, Cl_3 radicals will be more readily adsorbed on the walls than chlorine atoms and, with an over-all efficiency of 10^{-3}—10^{-4}, even a small absolute increase in their concentration will mean an appreciable rise in k_{12}, and therefore an appreciable fall in γ. The higher the incident intensity, the higher p_{Cl} and hence p_{Cl_3}, and the more pronounced this effect. At pressures of 13 and 45·7 mm. of chlorine, where n becomes 0·8—0·9, reaction (6)—and possibly (9)—commences to play a part, and ultimately preponderates. But reaction (12) persists, and only becomes insignificant under the conditions of high p_{Cl_2} and high intensity discussed earlier in this paper. In view of the known variability in catalytic properties of the walls, and of the assumed difference in ease of adsorption of Cl and Cl_3, any quantitative treatment of the results in this pressure region, involving both (6) and (12), is impossible.

The effects of added hydrogen chloride, in certain respects, resemble those of chlorine; both acceleration and retardation are observed, the former when the rates of reaction in absence of hydrogen chloride are low, whether owing to reactive vessel walls or to low intensity, and the latter when the velocities are high. In addition, accelerating effects are more marked at low chlorine pressures, and can change to a retardation as p_{Cl_2} increases (*e.g.*, Table V, Expts. 43, 45b, 46, 52). The accelerating effect, as in the case of chlorine, we attribute to the poisoning of the catalysed recombination of chlorine atoms taking place on the walls.* The action of hydrogen chloride in this respect is the stronger, as is revealed, not only by the seven-fold increase in γ shown by Expts. 46 and 51 as compared with 52 (Table III), but also by the results given in Table VI.

TABLE VI.

Expt.	Cl_2 mm.	$+ Cl_2$ mm.	+ HCl mm.	Relative γ.	Expt.	Cl_2 mm.	$+ Cl_2$ mm.	+ HCl mm.	Absolute γ.
13 (3)	1·7	+ 0·0	+ 0·46	1·0 *	25 (4)	1·7	+ 0·0	+ 0·26	11·1
12 (3)	1·7	+ 11·3	+ 0·12	0·75	24 (4)	1·7	+ 11·3	+ 0·0	12·2
22 (3)	1·7	+ 0·0	+ 11·0	1·04	29 (4)	1·7	+ 0·0	+ 10·9	31·4

* Absolute γ *ca.* 50.

The three factors which favour retardation by hydrogen chloride, *viz.*, walls of low catalytic power, relatively high p_{Cl_2}, and relatively high intensity, all imply relatively high values of p_{Cl}, and hence also of p_{Cl_3} and at a given $[Cl_2] : [H_2]$ ratio, of p_H. The first explanation to suggest itself is the possible occurrence of

$$H + HCl \longrightarrow H_2 + Cl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Everything indicates that k_{14} is of the order, not of k_3, as was deduced by Ritchie and Norrish (*Proc. Roy. Soc.*, 1933, *A*, **140**, 112), but rather of k_2 (Potts and Rollefson, *J. Amer. Chem. Soc.*, 1935, **57**, 1027; Rodebush and Spealman, *ibid.*, p. 1040; experiments of Sommer, quoted by Bodenstein and Winter, *loc. cit.*). With $k_3/k_{14} = 150$, the retarding effect of added hydrogen chloride would be given by the ratio $150[Cl_2] : (150[Cl_2] + [HCl])$, a relation which predicts 2—3% retardation where we observed 20—30%, and this in spite of the assumed superadded accelerating effect. The explanation we favour is that the added hydrogen chloride, by collision, stabilises the newly formed Cl_3 radicals, and that, as already argued, these radicals are adsorbed more easily by the vessel walls than are chlorine atoms. The remarkable decrease in the slope sometimes observed at very low hydrogen pressures in presence of hydrogen chloride (see Part V) is to be ascribed to the same effect. In one case (Table III; Part V, Table II, Expt. 73), where 318 mm. of hydrogen chloride caused a very considerable lowering of γ at $p_{Cl_2} = 13$ mm., this was accompanied by a fall in n to the unusually low figure of 0·72, indicating extensive recombination of Cl_3 radicals in the gas phase. The total heat liberated in the illuminated zone was small, and consequently also the convection effect, and doubtless the main function of the added gas was to restrict diffusion, and thus maintain a relatively high concentration of Cl_3 in and near the centre of the reaction vessel.

Comparison with results of other workers. Any contradiction between our results and those of Bodenstein and Winter is merely apparent. They worked with reaction mixtures in which either hydrogen and chlorine pressures were of the same order, or excess of hydrogen was present. The maximum value of the ratio p_{Cl_2}/p_{H_2} quoted is 1·9 and the minimum as low as 0·02, whilst at 375 mm. of chlorine, their rates of quantum absorption appear to

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* This wall poisoning by chlorine and by hydrogen chloride in the present reaction runs quite parallel to the corresponding results in the case of the rate of combination of bromine atoms on the walls of the containing vessel, in absence and in presence of bromine and hydrogen bromide (Schwab, *Z. physikal. Chem.*, 1934, *B*, **27**, 452; Hilferding and Steiner, *ibid.*, 1935, **30**, 399).

have been about 10^9 per c.c. per sec. In our later work, on the other hand, p_{Cl_2}/p_{H_2} varied between limits of about 300 and 30,000, and the rates of quantum absorption, referred to the whole cell, not merely to the insolated zone, fell between $10^{10 \cdot 2}$ and $10^{13 \cdot 4}$ per c.c. per sec. when p_{Cl_2} was 166 or 450 mm. Both the p_{Cl_2}/p_{H_2} ratio and also the stationary chlorine-atom concentration were far higher in our experiments; *i.e.*, the conditions were such as to favour

$$(4)\ Cl + Cl_2 \longrightarrow Cl_3\ (k_4 = 10^{19 \cdot 74}\text{ molecules c.c.}^{-1}\text{ sec.}^{-1}\text{ mm.}^{-2})$$

rather than

$$(2)\ Cl + H_2 \longrightarrow HCl + H\ (k_2 = 10^{19 \cdot 46}\text{ molecules c.c.}^{-1}\text{ sec.}^{-1}\text{ mm.}^{-2})$$

and, moreover, to furnish a relatively high stationary Cl_3 concentration, the equilibrium $Cl + Cl_2 \rightleftarrows Cl_3$ being assumed to be set up. In Bodenstein and Winter's experiments, the chances of this last being the case were very slight, and in any case, the resulting Cl_3 concentration would be too low to cause appreciable chain ending by (6) as compared with (12). In the matter of the part played by the vessel walls, we are in agreement with these authors, as also with their brief reference (*loc. cit.*, p. 18) to certain experiments on the effect of hydrogen chloride (" sometimes no change in velocity, sometimes a retardation, and occasionally an acceleration "), except that, under our conditions, an acceleration was observed more often than otherwise.

Potts and Rollefson obtained results at room temperature essentially agreeing with those of Bodenstein, *i.e.*, in accordance with (12), but with evidence of slight systematic retardation by reaction (14). At 167° K., however, their data are expressed by an equation which, rewritten, becomes

$$\gamma = k[H_2]/I_{abs.}^{0 \cdot 5} \qquad (15)$$

formally identical with our expression (8), the first power of the chlorine concentration in the denominator being omitted. The room-temperature measurements involved chlorine and hydrogen pressures varying respectively between about 11—22 mm. and 7—17 mm. Under our conditions, we should have expected for such pressures of chlorine an intensity exponent of about 0·85—0·9, whereas one of unity was found. This is readily explained by the fact that Potts and Rollefson used hydrogen pressures about 100 times as great as those employed by us, with a resulting low value of p_{Cl_3}. In the measurements at 167° K., the ratio p_{H_2}/p_{Cl_2} was $\sim$ 3—4 as compared with $\sim$ 1 at 290° K. Using, as before, 5·94 kg.-cals. and 5·0 kg.-cals. respectively for E_2 and E_4, we calculate, however, that the ratio of the reduction in rate of these two processes on passing from 290° to 167° K. is about 3·3 : 1, and consequently the relative numbers of successful Cl–H_2 and Cl–Cl_2 collisions will be practically the same in the experiments carried out at the two temperatures. On the other hand, K_7 increases as the temperature falls. With $\Delta H = -\ 2 \cdot 5$ kg.-cals. for (4), we calculate that the equilibrium ratio p_{Cl_3}/p_{Cl} at 167° K. will be 24-fold its value at room temperature, and it is to this fact that the change in the value of n must be attributed. The experimental method used by Potts and Rollefson did not allow of any independent variation of p_{Cl_2}; the pressure of chlorine actually used will be included in their k value. Ritchie and Norrish used at any given chlorine pressure (*e.g.*, 44 mm. as in their Tables I and III) much the same total rate of quantum absorption as we did. On the other hand, their reaction cell was of volume 25·4 c.c., as compared with our 491 c.c., and the rate of quantum absorption per unit volume consequently 20 times as great. Their values of n were well below unity,* and, in view of the high hydrogen pressures (*e.g.*, 44 mm.) employed, this can only have been the consequence of the very high stationary chlorine-atom and Cl_3 concentrations resulting from the high rate of light absorption, combined with the presence of cell walls very efficiently poisoned in respect of chlorine-atom recombination. The effect of p_{Cl_2} on γ over the range 12—90 mm. was much as observed by us. They also found a marked and progressive retardation when p_{HCl} was increased from 12·5 to 317 mm. in a

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* According to them, 0·6; but whilst this fits their results at 67 mm. of chlorine, the data at 44 mm. are better expressed by a figure of 0·7.

mixture containing 44 mm. each of hydrogen and of chlorine, and attributed it to the occurrence of reaction (14). They did no measurements on the effect of adding smaller quantities of hydrogen chloride. Whilst we cannot agree with this interpretation of their results, it should be remarked that we observed similar effects in a few isolated experiments (Table III), and have ascribed them to enhanced concentrations of Cl_3.

SUMMARY.

(1) Quantum yields varying between 0·05 and 2000 are calculated for the experiments recorded in Parts V and VI. Depending on the conditions, they either pass through a maximum at some intermediate chlorine pressure, or, in a few cases, decrease continuously as the chlorine pressure increases. At high intensities and pressures of chlorine, they vary under the conditions of experiment in accordance with the inverse square power of the chlorine pressure.

(2) Experiments on the effect of added hydrogen chloride are tabulated and discussed.

(3) Suggestions are put forward to explain the experimental results. Reaction chains are ended by the disappearance of chlorine atoms and of Cl_3 radicals, both on the walls and, without triple collisions, in the gas phase. The rôles played by non-uniform illumination, convection, and diffusion are estimated.

(4) The results are compatible with those obtained by other workers on the same reaction.

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