396. *The Photochemical Union of Hydrogen and Chlorine. Part V. The Reaction at Low Pressures. The Effect of Light Intensity in the Absence of Oxygen.*

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(*General Summary of Parts V and VI.*)

The objects of this work were the investigation of the experimental laws governing the kinetics of the photochemical reaction between hydrogen and chlorine in absence of oxygen, and the deduction of a mechanism for it. Existing data were very discordant,

some workers finding proportionality between rate and $I_{\text{abs.}}$, others between rate and $I^{0\cdot5}_{\text{abs.}}$, whilst Rollefson obtained both relations by variation of the experimental conditions. All were agreed that rate is proportional to hydrogen pressure. We therefore used a method (employed in Part IV but not described) which, whilst limiting our experiments to low hydrogen pressures of the order of 0·1 mm., had advantages from other points of view. Apparatus and technique are described in some detail, and certain points submitted to a critical examination, necessary in view of the unusual nature of the results obtained. In the actual experiments, we worked at eight chlorine pressures, spaced between the limits 0·012—450 mm. A few experiments were done on the effects of added hydrogen chloride. Incident intensities were altered over ranges varying between 2 : 1 and 1600 : 1. Measured velocities varied between extremes of 800 : 1, and calculated quantum yields, referred to hydrogen, over the range 0·05—2000.

The results showed that the exponent n in the equation, rate $= k \, . \, I^n$, could vary over the range 0·05—1, the latter figure being found at low chlorine pressures, and the values becoming lower as light intensity and chlorine pressure were increased. At sufficiently high pressures, there was an intensity range over which n, within experimental error, was 0·5. A second, remarkable result, not hitherto recorded, was that rate of reaction and, more markedly, quantum yield passed through a maximum as p_{Cl_2} was increased, and then fell off more and more rapidly, until the quantum yield varied as $p^{-2}_{\text{Cl}_2}$. The influence of added hydrogen chloride was complex, but could be analysed into superposed accelerating and retarding effects.

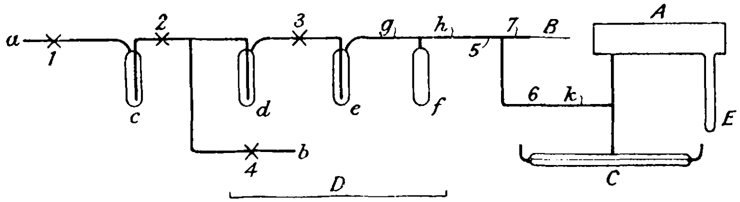
The results are explained by assuming the existence of the radical Cl_3, already postulated in Part IV to account for the effect of wave-length on quantum yield. Its maximum concentration would be controlled by the equilibrium $\text{Cl} + \text{Cl}_2 \leftrightarrows \text{Cl}_3$, assumed to be set up under certain conditions, but more usually not reached. An intensity exponent of unity denotes that the reaction chains are terminated by adsorption of Cl atoms and of Cl_3 radicals on the walls of the vessel. The efficiency of these wall collisions is low, and is depressed still further by adsorbed chlorine and hydrogen chloride. Values of n between 1 and 0·5, found under conditions where three-body collisions are rare events, are due to the gaseous reactions $2\text{Cl}_3 \longrightarrow 3\text{Cl}_2$ and, probably, $\text{Cl} + \text{Cl}_3 \longrightarrow 2\text{Cl}_2$. Values of n less than 0·5 are the result of localised illumination, and of retarded diffusion of chlorine atoms out of this zone into the dark space in the cell. The kinetic effect of chlorine is, in part, a consequence of the assumption of Cl_3 formation, and the enhanced effects found at high pressures and intensities are due to the same retarded diffusion just mentioned. The suggested mechanism, whilst involving some modification of the results of the quantum-mechanical treatment of the $\text{Cl—Cl}_2\text{—Cl}_3$ equilibrium by Rollefson and Eyring, appears to be consistent with reported results of other workers, using different experimental conditions.

EXPERIMENTS carried out by Craggs during 1930—1933, already briefly referred to in Part IV (J., 1936, 241), and now to be quoted in more detail, had shown that, in absence of oxygen and at hydrogen pressures of the order of 0·1 mm., the intensity exponent (n in the expression, rate $\propto I_0{}^n$) was practically unity at the lowest chlorine pressures used, but decreased continually as p_{Cl_2} increased, the lowest value recorded being 0·68 at 166 mm. of chlorine. Such a tendency was in accord with the prediction originally made by Chapman (*Trans. Faraday Soc.*, 1925, **21**, 547) and also with the published note of Chapman and Grigg (*Nature*, 1931, **127**, 584) and the work of Ritchie and Norrish (*Proc. Roy. Soc.*, *A*, 1933, **140**, 112); but it was directly opposed to the results of Bodenstein and Unger (*Z. physikal. Chem.*, 1931, *B*, **11**, 253), to those obtained at room temperature by Potts and Rollefson (*J. Amer. Chem. Soc.*, 1935, **57**, 1027), and to those published by Bodenstein and Winter (*Sitzungsber. preuss. Akad. Wiss.*, 1936, 1) whilst our own experiments were in progress. In addition, Craggs showed that, above a certain point, increase in p_{Cl_2} markedly retarded the reaction under his conditions of work, whereas neither Bodenstein nor Rollefson noted any such effect. Craggs was controlling his chlorine pressure by immersion of a side limb of the apparatus, containing liquid or solid chlorine, in a constant-temperature bath of refrigerant. If the chlorine condensate were to contain a trace of some volatile inhibitor, this fact would, of course, explain the retardation referred to. But in addition, and as a consequence of the mechanism of chain termination common to all such inhibitors, the intensity exponent n

would tend to rise with increasing p_{Cl_2}, and finally approach once more a value of unity. The trend of the n–p_{Cl_2} graph of Craggs' experiments did, in fact, not exclude such a possible result of a further increase in chlorine pressure. We consequently undertook extensive experiments in order to clear up these points; the results fully confirm those of Craggs, and demonstrate that the marked retarding effect shown by chlorine cannot be due to any adventitious inhibitor.

EXPERIMENTAL.

The technique employed in all this work, including the experiments described in Part IV, was based on that devised by Rollefson (*J. Amer. Chem. Soc.*, 1929, **51**, 770). The apparatus used, modified in minor details from time to time, consisted essentially of an insolation vessel (*A*), provided with means of introducing hydrogen (*B*) and measuring its pressure before and after reaction (*C*), of introducing chlorine (*D*) and regulating its pressure during the reaction, and of condensing out hydrogen chloride and chlorine after the reaction (*E*). The figure shows diagrammatically the form used in the experiments of 1935—1936. Evacuation was effected through *a* by means of a mercury diffusion pump backed by a Hyvac pump. The trap *c*, immersed in liquid air, protected the apparatus from mercury vapour and the pump from chlorine; 1, 2, 3, and 4 were mercury-sealed taps lubricated with metaphosphoric acid in accordance with instructions kindly communicated by Mr. D. L. Chapman. Before being turned, they were warmed to about 50° by means of an electrically heated coil of wire wound round the barrel. In the earliest experiments, similar taps were also inserted at points 5 and 6, but they were eliminated later, as they were found to cause trouble during long-continued runs.



A was a cylindrical quartz vessel with plane ends (25 cm. × 5 cm. diameter). Connection with the glass parts of the apparatus was made by quartz–soda glass fused joints; *B* was a small palladium tube sealed on to glass by means of a platinum junction. Hydrogen passed readily through this when heated in a small Bunsen flame. If larger quantities were required, the palladium was jacketed by a quartz tube, hydrogen passed through the annular space, and the whole heated in a Bunsen flame. Special experiments showed no appreciable reaction to take place between the chlorine and the palladium, nor any combination of hydrogen and chlorine to be caused by the palladium surface. *C* was a Pirani gauge with a glass-covered mercury thread, constructed according to Rollefson (*loc. cit.*, p. 804). This proved very satisfactory in use. The glass capillary was about 20 cm. long, and its containing tube about 10 mm. in diameter. The resistance of the mercury thread at room temperature was of the order of 20Ω, and, with the balancing resistances used, the reaction system evacuated, and liquid air around *E*, some 3—4 volts (the zero voltage v_0) were necessary across the bridge for a balance with different gauges. This figure sometimes showed variations of the order of 0·04—0·08 volt from series to series, probably due to the effect of baking out on a minute gas bubble present in the mercury thread. With hydrogen gas in the system, a higher voltage v was required. When compared against known hydrogen pressures, by means of a McLeod gauge, the plot of p_{H_2} against $f(v) = (v^2 - v_0^2)/v_0^2$ was slightly concave to the pressure axis; v_0 was found to vary with temperature, and the gauge was consequently kept at a constant temperature by means of a water-jacket. The estimated errors in the pressure values were of the order of 0·002 mm. at 0·2 mm. and 0·0005 mm. at 0·02 mm. At still lower pressures they were relatively greater, as the voltmeter used could only be read to 0·01 volt.

For *D*, a cylinder of liquid chlorine, provided with a silver-lined needle valve, was sealed on at *b* by means of a metal–glass joint. With the apparatus evacuated, tap 2 closed, and liquid air on *d*, chlorine was admitted and permanent gas pumped off. The chlorine was then distilled into *e* and back again into *d*, the head and tail fractions, in all about half of the original condensate in *d*, being collected in *c*. This procedure was repeated, and the final middle fraction from *e* transferred to *E*, and used for the actual experiments. Towards the end of the work, a modified technique was employed. The chlorine, after fractionation, was distilled from *e* into *f*, and a capillary constriction at *g* sealed off. Melting chlorobenzene (m.p. 228° K.) was placed round *f*. After sufficient time had been allowed for the apparatus to become filled with chlorine at 450 mm. pressure (the vapour pressure of liquid chlorine at 228° K., see Table I), the reaction zone was sealed off at *h*. By working in this way, no chlorine condensate was present during experiments at 450 mm. of chlorine, and only minimum amounts when using lower values of p_{Cl_2}.

E consisted of a tube of 9 mm. internal diameter sealed on to *A*. During an experiment, its lower end was immersed in a bath of some half-molten refrigerant of known m. p., the chlorine pressure inside the reaction space thus being kept constant. Great care was taken to ensure the purity of the liquids used. Their m. p.'s (from I.C.T.) and the corresponding chlorine pressures interpolated from Harteck's data (*Z. physikal. Chem.*, 1928, **124**, 21) are contained in Table I.

TABLE I.

Refrigerant.	Temp. (° K.).	Pressure (mm.).	Refrigerant.	Temp. (° K.).	Pressure (mm.).
Allyl chloride	136·6	0·012	Ethyl acetate	189·6	45·7
Methyl*cyclo*hexane	146·6	0·11	Ethyl propionate ...	199·3	82·6
Carbon disulphide ...	161·4	1·7	Chloroform	209·7	166
Toluene	178·5	13·0	Chlorobenzene	228	450

It was found necessary to stir the refrigerant frequently to maintain it at a constant temperature as measured by a platinum resistance thermometer, and where very long runs were concerned a method was devised of syphoning more liquid air on to the refrigerant at regular intervals. Sleeve-like insertions of black cloth in the sides of the light-tight box enclosing the reaction system allowed of these and other necessary manipulations. When a measurement of hydrogen pressure was being taken before and after an experiment, *E* was immersed in liquid air up to a fixed depth, and the gauge reading recorded when constant. Preliminary experiments showed condensed hydrogen chloride to exert, at liquid-air temperature, a pressure equivalent to 0·0018 mm. of hydrogen on the Pirani gauge. The corresponding correction was made when required.

In carrying out a series of experiments, the apparatus was first baked out and evacuated in the usual way until the gauge reading was constant. Chlorine was admitted as described, the apparatus sealed off at *h*, liquid air adjusted around *E*, and v_0 read off. After hydrogen had been admitted, and its initial pressure read, the liquid air around *E* was replaced by the constant-temperature bath giving the required chlorine pressure and, after 20 mins'. standing (10 mins. used in the earlier experiments were found to be insufficient to secure uniformity of hydrogen pressure throughout the apparatus), insolation was commenced. At its conclusion, liquid air was replaced around *E*, and the new pressure reading taken. The apparatus was then ready, after readjustment of the chlorine pressure, for another insolation. More hydrogen was admitted, as and when required, through *B*. The supply of chlorine present at the start in *E* sufficed for all the experiments required in a particular series of runs. Hydrogen chloride accumulated in the apparatus, its amount at any instant being known from the total quantity of hydrogen which had been consumed. In the earlier experiments, before the procedure of sealing off at *h* was adopted, it was removed by evacuation as required. Higher hydrogen chloride pressures were obtained by the admission, in stages, of the calculated pressure of hydrogen and its photocombination with chlorine.

The apparatus used in the experiments of 1930—1933, in addition to quartz, sometimes employed reaction vessels (*A*) of glass (24—27 cm. × 2·7—2·9 cm. diameter). In some experiments, a tap was inserted at 7, the palladium tube *B* thus at no time coming into contact with chlorine. In others, after filling with hydrogen, the reaction space was sealed off at *h*. Whilst the first precaution was subsequently shown to be unnecessary, the sealing off of the reaction zone, as already mentioned, was certainly advantageous.

In the later work, we used as light sources a 1000-watt metal-filament lamp and a quartz–mercury arc, both running on the 100—110 volt constant-voltage circuit, the light being passed through a blue Corning glass filter (G 40 d), of which the spectral transmission had been carefully measured at intervals of 100 A. The maximum figure lay at 5000 A. The beam was rendered approximately parallel and of the required diameter by means of two quartz lenses and diaphragms before entering the cell, and, on leaving, was concentrated by means of a third lens on a calibrated 2-cm. Moll surface thermopile, the *E.M.F.* produced being measured by a micro-potentiometer. Various devices were employed to reduce the intensity. A "neutral" wedge *

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* This proved to have considerable selective absorption, which made impossible any quantum-efficiency calculations. On this account, its use was discontinued.

(see Part I; J., 1930, 2694) was first used in conjunction with the metal-filament lamp, and in experiments with the mercury arc, an adjustable sector diaphragm on the first lens. In order to secure a more considerable variation in intensity, copper-gauze screens were found to be the most convenient, as many as four being clamped together for the lowest intensities, and they were exclusively used at the end of the work. In all cases, the intensity reduction was directly measured by means of the thermopile and either potentiometer or galvanometer. The earlier experiments employed a quartz–mercury arc, together with 1000-watt and 100-watt metal-filament lamps. The usual filter was a soda-glass plate. The light flux was varied by the sector diaphragm method, the intensity ratio being determined as above.

It should be emphasised that insolation was always effected by a beam of light passing axially down the centre of the cell. Its diameter varied, but in no case was the whole cross-section of the reaction cell illuminated.

Before passing to detail, certain general features of the results will be considered. In agreement with Rollefson, it was found that the reaction is essentially of the first order with respect to hydrogen, and that therefore a plot of log p_{H_2} against time of insolation tends to be linear. The expression $100(-\Delta \log p_{H_2})/t$, where p_{H_2} is expressed in mm. and t in minutes, will be termed the *slope*, and, at constant incident intensity, is a measure of the effect of chlorine and of hydrogen chloride on the rate, or, when divided by the corresponding rate of quantum absorption, on the quantum efficiency. Favourable examples of the degree of constancy of slope found in a single experiment follow.

Expt. 24.

Cl_2, 13·0 mm.; initial HCl, 0·00 mm.

t.	p_{H_2}.	Slope.
0	0·1315	3·34
3	0·1044	3·15
10·5	0·0606	3·46
20·5	0·0273	3·88
35·5	0·00715	3·40
55·0	0·00155	

Mean value of slopes .... 3·45
Mean slopes over whole run... 3·51

Expt. 53.

Cl_2, 1·7 mm.; initial HCl, 0·10 mm.

t.	p_{H_2}.	Slope.
0	0·0925	4·13
7	0·0475	3·89
17	0·0194	4·00
28	0·00705	3·81
37	0·0032	

Mean value of slopes .... 3·96
Mean slope over whole run ... 3·95

Expt. IX, e.

Cl_2, 45·7 mm.; initial HCl, 2·485 mm.

t.	p_{H_2}.	Slope.
0	0·1805	5·22
5	0·0990	5·24
10	0·0541	4·89
15	0·0308	5·12
20·5	0·0161	(4·22)
25·5	0·0099	

Mean slope .... 5·12

Expt. X, g.

Cl_2, 166 mm.; initial HCl 1·16 mm.

t.	p_{H_2}.	Relative intensity.	Slope.
0	0·1633	5·65	3·26
5	0·1122	1·00	1·62
10	0·0931	1·00	1·63
15	0·0772	5·65	3·08
20	0·0541		

Mean slopes .... 3·17 and 1·625
Value of n .... 0·39

Frequently, the concordance inside a given run was, however, less good, and the slopes showed irregular variations of the order of 15—20%. The causes of these fluctuations were, we think, two-fold—on the one hand, variations in catalytic power of the walls of the reaction vessel and in the degree of convection taking place in the reacting gases, and, on the other, changes in temperature of the condensed chlorine in *E* (see fig.). One other apparent anomaly must be mentioned. In a number of cases, when hydrogen chloride was present, the slope fell off as the hydrogen pressure became very low. The most striking examples were the following, for which an explanation is offered in Part VI.

Expt. 21.

Cl_2, 13·0 mm.; initial HCl, 10·8 mm.

t.	p_{H_2}.	Slope.
0	0·0154	6·70
7	0·00523	1·87
18	0·00326	

Expt. 46.

Cl_2, 0·012 mm.; initial HCl, 6·9 mm.

t.	p_{H_2}.	Slope.
0	0·260	1·60
40	0·0595	1·76
78	0·0127	0·67
101	0·0089	

Expt. 48.

Cl_2, 1·7 mm.; initial HCl, 46·2 mm.

t.	p_{H_2}.	Slope.
0	0·246	11·9
4	0·0825	12·3
9	0·0200	7·51
12	0·0119	6·07
19	0·00447	

Two further points must be referred to, which concern in principle the validity of our experimental method, *viz.*, the facts that (i) the closed system is not at a uniform temperature during an insolation, the temperature gradient being accentuated during the measurement of hydrogen pressures, and (ii) during reaction, hydrogen will arrive in the insolated zone from the rest of the apparatus by diffusion and convection. We have gone very fully into the possibility that the values of our slopes might be falsified by these two circumstances, and have concluded that any errors are of a minor order. The correction involved in the first case becomes very small when the fact that the volume of the cooled zone is perhaps 5% of the total volume is taken into account. Direct observations on the rate and extent of pressure change taking place when the end of E is immersed in liquid air, when one refrigerant is replaced by another, and when hydrogen is admitted to the reaction zone with liquid air on E all confirm the conclusion that any error can be neglected. With regard to the second point, we are assuming that, for all practical purposes, p_{H_2} is constant throughout the whole apparatus at any moment. In the later experiments, the approximate volumes of the different parts of the apparatus were: reaction cell (central portion only illuminated), 490 c.c.; side tube E, 80 c.c.; Pirani gauge and remainder of system, 90 c.c. Similar relations held in the earlier experiments. Quite apart from convection, which played an important rôle at all save the highest chlorine pressures, calculation of diffusion rates shows that the hydrogen content of E would not differ appreciably during the insolation from that in the reaction cell. The case of the Pirani gauge with its associated lengths of 5-mm.-bore tubing is more difficult, and it is best here to consider the general nature of the results of all the experiments. If the observed slopes are in error owing to retarded diffusion of hydrogen, it can be shown that, in any insolation, the effect will be greater (i) the greater the ratio p_0/p of the initial to the final pressure, (ii) the higher the chlorine and hydrogen chloride pressures, (iii) the greater the rate of reaction of hydrogen (high intensities and gas sensitivities), and (iv) the lower the initial hydrogen pressure. *No such correlation is visible in our data.* We conclude that, whilst there must necessarily have been a hydrogen-pressure gradient in the reaction system during our experiments, hydrogen passed sufficiently rapidly from the dead space into the reaction zone to avoid any serious distortion of the results.

Results

In what follows, the later (1935—36) experiments are denoted by series numbers and letters, *e.g.*, VII, c; IX, f; and the earlier ones (1930—33) by numbers with the number of the series in parentheses, *e.g.*, 29 (4); 36 (7). Table II comprises all the data for chlorine pressures up to 13 mm., Table III the earlier results with 45·7 and 166 mm., and Table IV the more recent data obtained at such higher pressures; W and Hg denote respectively metal-filament and mercury-arc lamps. The difference between Σp, the total pressure, and p_{Cl_2} is accounted for to the extent of about 0·1 mm. by hydrogen, the remainder being hydrogen chloride. In Table IV absorbed intensities are given in quanta per second, calculated from thermopile deflexions obtained with the empty cell, the energy distribution in the light source, the measured filter transmissions, and the known extinction coefficients of chlorine. In the case of the mercury-arc radiation, the only two lines transmitted by the filter and appreciably absorbed by chlorine were 4050 and 4360 A. In the case of the tungsten-filament lamp, which burnt at about 3040° K., the maximum quantum intensity of the radiation transmitted by the filter lay at 5200 A., whilst the region of maximum quantum absorption by the chlorine moved from 4200 to 4400 A. as p_{Cl_2} increased from 45·7 to 450 mm. This statement refers essentially to the experiments of Series X; owing

TABLE II.

Expt.	p_{Cl_2} (mm.).	Σp (mm.).	Light source.	Filter.	Intensity ratio.	Mean slopes.	Slope ratio.	*n*.
58 (11)	0·11	0·97—1·30	W	None	10	0·22 : 0·024	9·2	0·96
VII, f	—	0·85—0·87	Hg	6 mm. soda glass	4·60	0·106 : 0·024	4·46	0·98
13, 15 (3)	1·7	2·4 —2·6	—	—	10	2·4 : 0·25	9·6	0·98
37 (7)	—	3·1	—	—	4·35	0·71 : 0·17	4·2	0·98
VII, c	—	2·1 — 2·2	—	—	4·60	1·22 : 0·24	5·1	1·06
VII, e	—	2·3 — 2·4	—	—	—	0·98 : 0·23	4·26	0·95
IX, f	—	5·0 — 5·1	—	—	5·45	1·54 : 0·32	4·81	0·93
12, 14 (3)	13·0	13·6 —13·8	—	—	10	11 : 1·4	7·9	0·90
30 (5)	—	13·2	—	—	4·35	7·8 : 2·0	3·9	0·93
31 (5)	—	13·1	—	—	—	6·9 : 1·8	3·8	0·91
36 (7)	—	14·0	—	—	—	5·2 : 1·4	3·7	0·89
VI, e	—	17·6	—	Corning G 40 d	4·60	1·99 : 0·57	3·5	0·82
73 (13) *	—	332	—	6 mm. soda glass	4·35	1·09 : 0·38	2·9	0·72

* In this experiment, there were present 318 mm. of HCl and also 0·075 mm. of O_2. This is the only occasion on which oxygen was present.

to the faulty nature of the " neutral wedge " employed in Series IV, as also in X, e and X, j, no absolute calculations can be made, and the region of maximum absorption will certainly lie at

TABLE III.

Expt.	p_{Cl_2} (mm.).	Σp (mm.).	Light source.	Filter.	Intensity ratio.	Mean slopes.	Slope ratio.	*n*.
32 (5)	45·7	46·1	Hg	6 mm. soda glass	4·35	13·0 : 3·7	3·5	0·85
34 (7)	—	45·9	—	—	—	11·8 : 3·7	3·2	0·79
35 (7)	—	46·3	—	—	—	10·4 : 3·3	3·2	0·79
38 (7)	—	55·9	—	—	—	10·7 : 3·2	3·3	0·81
129—131 (22)	—	46·6—46·7	—	*	1·93	0·886 : 0·562	1·58	0·70
39 (7)	166	176·5	—	6 mm. soda glass	4·35	3·5 : 1·2	2·9	0·70
41 (7)	—	177·4	—	—	—	3·0 : 1·1	2·7	0·68

* Radiation of wave-length 4360 A. was used in these experiments, employing a large monochromator. See Part IV.

TABLE IV.

Corning G 40 d filter in use throughout.

Expt.	Light source.	log quanta absorbed per sec.	Intensity ratio.	Mean slopes.	Slope ratio.	*n*.
		(*a*) p_{Cl_2} 45·7 mm.; Σp 47·3—49·2 mm.				
IV, i	W	? ?	4·49	2·58 : 0·63	4·10	0·94
V, c	Hg	14·051 : 13·678	2·36	4·66 : 2·38	1·96	0·78
V, d	—	13·299 : 12·926	—	0·93 : 0·42	2·21	0·92
V, e	—	13·299 : 12·926	—	1·33 : 0·63	2·11	0·87
V, f	—	13·299 : 12·926	—	1·26 : 0·55	2·29	0·96
VI, a	—	14·051 : 13·388	4·60	5·61 : 1·77	3·17	0·76
IX, e	—	14·051 : 13·299	5·65	5·12 : 1·23	4·16	0·82
		(*b*) p_{Cl_2} 82·6 mm.; Σp 84·1—87·8 mm.				
VI, d	Hg	14·249 : 13·586	4·60	6·69 : 2·72	2·46	0·59
VI, h	—	13·497 : 12·834	—	2·28 : 0·67	3·40	0·80
IX, a	—	14·249 : 13·497	5·65	4·67 : 1·22	3·83	0·78
IX, b	—	13·875 : 13·123	—	2·44 : 0·55	4·44	0·86
IX, c	—	13·497 : 12·745	—	1·25 : 0·28	4·46	0·86
IX, d	—	13·123 : 12·371	—	0·62 : 0·12	5·17	0·95
X, k	W	15·650 : 14·898	—	16·8 : 7·3	2·30	0·48
X, l	—	15·277 : 14·525	—	15·3 : 5·7	2·68	0·57
X, m	—	14·898 : 14·146	—	6·72 : 2·27	2·96	0·63
		(*c*) p_{Cl_2} 166 mm.; Σp 167·1—171·0 mm.				
IV, h	W	? ?	4·49	1·62 : 0·69	2·35	0·57
V, b	Hg	14·435 : 14·062	2·36	1·99 : 1·58	1·26	0·27
VI, g	—	14·435 : 13·772	4·60	3·15 : 1·86	1·69	0·34
IX, g	—	14·435 : 13·683	5·65	2·27 : 0·96	2·36	0·50
IX, h	—	14·061 : 13·309	—	1·32 : 0·415	3·18	0·67
IX, i	—	13·683 : 12·931	—	0·73 : 0·255	2·86	0·61
X, f	W	15·862 : 15·110	—	3·12 : 2·83	1·10	0·055
X, g	—	15·110 : 14·358	—	3·17 : 1·625	1·95	0·39
X, h	—	14·737 : 13·985	—	2·45 : 1·12	2·19	0·45
X, i	—	14·472 : 13·720	—	1·45 : 0·50	2·90	0·61
X, j *	—	? ?	—	0·37 : 0·093	4·0	0·80
		(*d*) p_{Cl_2} 447·5—450 mm.†; Σp 450·2—453·1 mm.				
IV, a	W	? ?	4·49	0·314 : 0·162	1·94	0·44
IV, g	—	? ?	—	0·314 : 0·161	1·95	0·44
V, a	Hg	14·585 : 14·212	2·36	0·364 : 0·286	1·27	0·28
VI, f	—	14·585 : 13·922	4·60	0·567 : 0·372	1·52	0·27
VI, i	—	13·833 : 13·170	—	0·309 : 0·177	1·75	0·37
VI, j	—	13·460 : 12·797	—	0·229 : 0·115	1·99	0·45
IX, j	—	13·833 : 13·081	5·65	0·076 : 0·027	2·81	0·60
X, a	W	16·095 : 15·343	—	0·83 : 0·72	1·15	0·081
X, b	—	15·343 : 14·591	—	0·79 : 0·43	1·84	0·35
X, c	—	14·970 : 14·218	—	0·53 : 0·26	2·04	0·41
X, d	—	14·737 : 13·985	—	0·39 : 0·175	2·23	0·46
X, e *	—	? ?	—	0·060 : 0·021	2·85	0·60

* The " neutral wedge " was used in X, e and X, j in order to reduce the intensities still further.

† The rates of quantum absorption in this section are, in all cases, those calculated for a chlorine pressure of 450 mm.

longer wave-lengths. Attention is drawn to the very high range of intensities covered in some of these experiments, more particularly in Series X, where the extreme values used when working with 166 and 450 mm. of chlorine were about 1000 : 1 and 1600 : 1 respectively. The highest and the lowest slope recorded in the tables are 16·8 and 0·021, a ratio of 800 : 1. These facts demonstrate the flexibility of the experimental method.

Discussion.

As already remarked, the observed slopes within a single experiment frequently showed variations of the order of 20%. Experiments in the same series, carried out under supposedly identical conditions [*e.g.*, Tables II and III, Expts. VII, c, e; 39, 41 (7); Table IV, Expts. IX, a—d; IV, a, g; X, a, b] show a degree of concordance which, although very variable, is of the same nature. If experiments in different series, *i.e.*, with different chlorine fillings, are compared, agreement is less good, the result of variations in catalytic properties of the cell walls. For example, the slopes in Series VI are always greater than those in Series V and IX, the latter approximating fairly closely to one another. The biggest discrepancy is that shown by Expts. VI, i and IX, j [Table IV (*d*)]. Moreover, for the same rate of quantum absorption, slopes in Series X are always less than those in the other series.

The first conclusion concerns the relation between p_{Cl_2} and n at constant incident intensity. The tendency found in the early experiments is fully confirmed by the later measurements, and it can be stated that, within the limits of experimental error, n falls continuously under our working conditions as p_{Cl_2} is increased up to the maximum of 450 mm. This is clearly shown in Table V, containing the results of all series of measurements in which three or more different chlorine pressures were experimented on at two identical incident intensities.

Table V.

Values of n.

	p_{Cl_2} (mm.).					
Expts.	1·7.	13.	45·7.	82·6.	166.	450.
34—39, 41 (7)	0·98	0·89	0·79—0·81	—	0·68—0·70	—
IV, a, g, h, i	—	—	0·94	—	0·57	0·44
V, a, b, c	—	—	0·78	—	0·27	0·25
VI, a, d, e, f, g	—	0·82	0·76	0·59	0·34	0·27
IX, a, e, g	—	—	0·82	0·78	0·50	—
IX, c, i, j	—	—	—	0·86	0·61	0·60
X, a, f, k	—	—	—	0·48	0·055	0·081
X, b, g, m	—	—	—	0·63	0·39	0·35

It will be noted that a figure of less than 0·5 is found even with 82·6 mm. of chlorine, that at 450 mm. this is the normal result, and that values below 0·1 are recorded.

No considerable variations of Σp as distinct from p_{Cl_2} are contained in Tables III and IV. In Table II, however, Expt. 73 shows the abnormally low n value of 0·72, which can only be due to the high pressure of hydrogen chloride. A small amount of oxygen was also present. This would not be expected to play any part at the low pressures of hydrogen employed, and if it were to affect the value of n, it would certainly raise, not lower it.

Table IV brings out the second main result, *viz.*, that in any given series of experiments [V in section (*a*); VI, IX, and X in section (*b*); IX and X in section (*c*); VI and X in section (*d*)], n decreases as the rate of absorption of light increases, the only exception being found in Expts. IX, h, i. The abnormally low values of n just referred to, where a 5·65-fold intensity increase only alters the reaction rate by 10—15%, are found at very high light intensities.

A further very important conclusion, which follows from an examination in Tables II—IV of the actual slopes found in the experiments mentioned in Table V, is that, at constant intensity, the rate of reaction passes through a maximum and then falls off as p_{Cl_2} increases.

The significance of these facts will be discussed in the succeeding paper, and one further point only will now be considered. The results show that n falls as the rate of light absorption increases. Obviously it is the absorption rate per unit volume which is significant. In the experiments of Table IV, employing polychromatic light of widely varying extinction coefficient, there are considerable differences between these rates at different depths in the reaction cell. These differences increase as p_{Cl_2} increases, and are more important for mercury than for tungsten radiation.

Table VI contains the percentages of the total quanta absorbed by the reacting gases, calculated for successive 5-cm. layers commencing from the front of the cell, for both filtered light beams, and for the four highest pressures used. In these, as in all other similar calculations, the radiation of the metal-filament lamp has been treated by dividing it up into sections each comprising 100 A., and using for each section the appropriate incident intensity and extinction coefficient. In this way, for example, it is calculated that, at 450 mm. of chlorine, the maximum intensity of the absorbed light lies, in the first 5 cm., at 4250—4300 A., but in the last 5 cm. at 4700 A.

TABLE VI.

Percentage distribution of absorbed quanta in 25-cm. reaction cell.

		1.	2.	3.	4.	5.
45·7 mm.	Hg	23·2	21·5	20·0	18·4	17·0
	W	22·6	21·3	19·8	18·7	17·6
82·6 mm.	Hg	25·8	22·4	19·6	17·1	15·1
	W	24·7	21·9	19·6	17·7	16·1
166 mm.	Hg	31·5	24·0	18·5	14·5	11·5
	W	28·8	22·9	18·9	15·9	13·6
450 mm.	Hg	49·0	24·8	13·6	7·9	4·8
	W	38·3	23·2	16·3	12·3	9·9

It is plain that the experimental value of *n* is an average figure for the whole reaction vessel, the true value increasing on passing from front to back. A comparison between the dependence of *n* on the absorbed intensity, as shown in Table IV, and the relative rates of quantum absorption in the first and the back layer, as given in Table VI, suggests that, in practice, this spatial variation of *n* should be negligible at 45·7 and 82·6 mm., perceptible at 166 mm., and very marked at 450 mm. Moreover, in the last case, it should be far more important for mercury than for tungsten radiation, the ratios for the absorption rates in the first and the back layer being 10·2 and 3·9 respectively. One would then expect that, at the same rate of quantum absorption, higher values of *n* should be obtained, working with 450 mm. of chlorine, when using the metal-filament lamp than when using the mercury arc. If, as before, we regard IX, j as an exceptional result, this is certainly so. It is also the case at 166 mm., and is plainly so at 82·6 mm., where no difference would be expected. Experiments from Series X are involved in all these comparisons, and it has already been mentioned that the slopes in this case, referred to the rates of quantum absorption, are relatively low. This being so, it is perhaps better to compare the *n* values for experiments with the two light sources which give approximately the same slope. When this is done, it is found that mercury-lamp experiments still give lower *n* values at 450 mm. (*e.g.*, V, a; VI, f; X, b, c, d: VI, i; IV, a, g; X, d), but that the differences at the other pressures are all plausibly covered by the errors of experiment and of comparison.

SUMMARY.

(1) The experimental technique employed in Parts IV—VI of this investigation is described, illustrated, and critically discussed.

(2) Results are tabulated of the effect of variation of intensity on the rate of reaction in oxygen-free hydrogen–chlorine mixtures, the hydrogen pressure being of the order of 0·1 mm., whilst the chlorine pressure varied between 0·11 and 450 mm.

(3) The intensity exponent *n* was found to vary between limits of 1 and 0·05, becoming less the higher the chlorine pressure and the higher the incident intensity.

(4) Under otherwise comparable conditions, lower values of *n* were obtained when using strongly absorbed (mercury arc) than when using weakly absorbed (tungsten filament) radiation.

(5) As the chlorine pressure increased at constant intensity, the rate of reaction passed through a maximum and then fell off.

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