52. *The Photochemical Union of Hydrogen and Chlorine. Part IV. The Reaction at Low Hydrogen Pressures. Effects of Wave-length, of Temperature and of Traces of Oxygen.*

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The work now described forms part of a more comprehensive study of the union of hydrogen and chlorine at low hydrogen pressures undertaken during the period 1930—1933. The experimental method will be described in detail later. It was similar to that devised by Rollefson (*J. Amer. Chem. Soc.*, 1929, **51**, 770) and used by Bateman and Craggs (*Trans. Faraday Soc.*, 1931, **27**, 445), the pressure of chlorine being kept constant throughout an experiment by the immersion of a side-tube of the apparatus, containing liquid or solid chlorine, in a bath of refrigerant, and the pressure of hydrogen being measured by means of a mercury-in-glass Pirani gauge, after chlorine and hydrogen chloride had been frozen

out by means of liquid air. Reaction vessels both of quartz and of glass were used. Chlorine was taken from a cylinder and distilled in a vacuum before being condensed in the reaction system. Its pressure was varied between 0·012 and 166 mm. Hydrogen was admitted by means of a palladium tube; its pressure was usually of the order of 0·1 mm.

The rate was found to be essentially proportional to the hydrogen pressure, and the effect of varying any particular condition was expressed in terms of its effect on the *slope*, this being defined as $-100\,(\Delta \log p_{H_2}/\Delta t)$, where p and t are in mm. and minutes respectively. The only other result which need be quoted at this stage is the effect of light intensity. Briefly, we found n, in the expression Rate $\propto I_0^n$, to be practically unity at the lowest chlorine pressures used, and to fall continually as p_{Cl_2} increased, the lowest value observed by us being 0·6—0·7 at 166 mm. of chlorine.

Experimental.

Reaction at 546 μμ.—Previous work with moist electrolytic gas at 1 atm. pressure containing traces of oxygen (Parts II and III, J., 1930, 2709; 1934, 157) had shown light at 546 μμ to be active in causing the combination of hydrogen and chlorine, in agreement with less specific conclusions of earlier workers. The mechanism of reaction in this region is not immediately obvious, and on that account it seemed desirable to test the point again under our modified experimental conditions, *i.e.*, working at low pressures of hydrogen and in absence of oxygen. The preliminary experiments were done by using a similar compound filter to that employed in Part II (*loc. cit.*, p. 2711). The light source was a 100-volt quartz-mercury lamp, used without any diaphragm in order to get the maximum available intensity. The results were inconclusive, in that, whilst a definite reaction was obtained, the use of an additional filter showed that traces of light of shorter wave-length than 546 μμ were also present. It was therefore decided to work with the large monochromator used in Part III. A series of careful preliminary measurements was first carried out, in which the prism drum of the monochromator was set at various readings adjacent to those corresponding to the different mercury lines, and the values plotted against the deflexions given by a combination of a linear thermopile, placed in an air-tight case behind the telescope slit, and a Zernicke moving-coil galvanometer. The light source was a 200-volt vertical atmospheric mercury arc, the radiation being concentrated on the collimator slit by means of a quartz lens. The relative intensities of the mercury lines were estimated in this way, and an idea obtained of the magnitude of the stray light energy which might be expected to be present when using the instrument. This proved to be small, as the following typical examples show:

313 μμ.		546 μμ.	
Drum reading.	Deflexion, mm.	Drum reading.	Deflexion, mm.
672	5	846	10
678	575 (maximum)	851	1120 (maximum)
685	5	855·5	15

Similar results were obtained in all other cases, and indicate that the proportion of stray light to be expected when working with one of the mercury lines is about 1%, distributed over the whole of the spectrum. This proportion is insufficient to affect the measurements recorded later of relative quantum yield except (see remarks on Expts. 84—88 below) when the extinction coefficient of the gas for the wave-length under investigation is particularly low.

In the experiments which follow, the usual quartz apparatus was employed, completely sealed off from pump and palladium tube after introduction of the gases. The prism drum was set to 546 μμ. The linear thermopile was removed from the telescope slit, and the emergent light converted by a cylindrical quartz lens into a beam which passed through the reaction vessel. The small percentage of stray light in the beam was still further reduced by the use of two filters, chosen to cut out all light below 546 μμ. Of these, I transmitted 59·4% at 546 μμ, and II, which also cut out yellow and red light, 11%. Neither passed detectable amounts at 436 μμ. The results are summarised in Table I. The figures in parentheses in the last column denote slopes which are zero within the experimental error.

Expts. 81—83*a*, in which the slope decreased as the monochromator setting moved towards the blue, show very clearly that the action at 546 μμ is not due to stray light of short wave-length, but to the mercury-green line itself, a conclusion confirmed by Expts. 90—93. In the

TABLE I. (Series 16.)

Expt.	Filter.	Monochromator setting, μμ.	Cl_2, mm.	HCl, mm.	Initial H_2, mm.	Final H_2, mm.	Total time, mins.	Mean slope.
81	I	546	45·7	0·00	0·605	0·545	784	0·0058
82	I	520	,,	0·12	0·545	0·540	438	0·0009
83	I	492	,,	0·12	0·540	0·538	266	(0·0006)
83*a*	I	436	,,	0·12	0·538	0·538	257	zero
84	None	546	,,	0·12	0·538	0·4345	291	0·0319
85	None	520	,,	0·34	0·4345	0·404	117	0·0270
86	None	534	,,	0·40	0·404	0·379	113	0·0246
87	None	492	,,	0·44	0·379	0·340	104	0·0467
88	None	436	,,	0·52	0·340	0·2145	4	5·0
89	I	546	166	0·86	0·1726	0·1668	321	0·0046
90	II	436	45·7	0·90	0·1480	0·1479	150	(0·0002)
91	II	546	,,	0·90	0·1479	0·1457	416	0·0016
92	I	546	,,	0·90	0·1457	0·1425	185	0·0052
93	I	492	,,	0·90	0·1425	0·1424	195	(0·0002)

absence of a filter, Expts. 84 and 86 show the same tendency; but the slopes then begin to rise as the monochromator is set at shorter wave-lengths. This in undoubtedly due to the stray light which, although present in small quantity, will be relatively very strongly absorbed in this region (absorption at 366 μμ, 405 μμ, 436 μμ, and 546 μμ respectively about 98, 42, 20, and 0·03%). Most of the reaction in Expt. 84 must be attributed to this 1% of stray light. This is confirmed by the fact that, whilst the transmissions of Filters I and II at 546 μμ are 59·4 and 11%, the corresponding slopes in Expts. 81, 92, and 91 are respectively only about 18, 17 and 5% of that in Expt. 84. In the relative measurements of γ, described later, this stray light effect will play quite a minor part (except when working with 546 μμ); the difference between its average extinction coefficient and that of the light rays actually under study is far smaller than, indeed of quite a different order from, that in the present case. The ratio of the slopes in Expts. 81 and 91 corresponds to an n value of 0·76, and that of Expts. 91—92 to $n = 0·70$. The value deduced earlier for white light at this pressure was 0·76. Taking this figure as a basis, we can calculate that about three-quarters of the observed reaction in Expt. 84 was due to stray light.

Reaction at 579 μμ.—Between Expts. 88 and 89, two experiments were carried out in the same way as above, using the monochromator in conjunction with a yellow Corning filter G.34R, which transmits only 1% of the 546 μμ line. At 45·7 mm. of chlorine, the slope over a 2-hour period was zero within the experimental error. At 166 mm. there was a very doubtful reaction in 11 hours (no pressure change during two out of the four time intervals into which the experiment was divided). Any reaction at 579 μμ would be expected to have a very high temperature coefficient. Consequently, an experiment lasting 22 hours was done with 45·7 mm. of chlorine at 57° by the methods described below. Again, the slope was practically zero, and *less* than in the experiment at room temperature. We conclude therefore that, although all three experiments gave very slight pressure decreases (severally 0·0005, 0·0052, and 0·0013 mm.), these are due to erroneous pressure readings, and that light of this wave-length is inactive.

Effect of Temperature at 436 μμ *and* 546 μμ.—Earlier work, both experimental and theoretical, had indicated that the temperature coefficient in green light, reaction being assumed to take place, would be considerably higher than that in the continuous spectrum region. The experiments just described show conclusively that the reaction can proceed in monochromatic light of λ 546 μμ, and we consequently undertook measurements of the temperature coefficient at this wave-length and at 436 μμ, which lies well within the continuum. For this purpose, the reaction vessel was jacketted by a thin copper sheet projecting about 4 cm. beyond the ends of the cell, then wound with a uniformly spaced coil of resistance wire and covered with a thick layer of asbestos string. A thermometer inserted in a socket in the copper jacket indicated the temperature of the cell, which was heated electrically to about 57°, at which temperature it could readily be kept constant by slight adjustments of an external resistance. Three experiments were done with 546 μμ light, alternating with two at room temperature. These were followed by similar experiments with the 436 μμ line. When working at 57°, the cell, subsequently to Expt. 97, was kept at this temperature for at least 12 hours prior to illumination, as in this case the slope rose considerably during the first few insolations and was still rising at the end, suggesting that temperature equilibrium had not been reached. This was not observed at room temperature. All experiments were carried out at $p_{Cl_2} = 45·7$ mm., and Filter I was used when working with 546 μμ. In Expts. 97—101 (duration of insolation, 5—20

hours) the slopes given are the final ones observed. In Expts. 102—104, lasting a few minutes only, the slopes are the average figures. The results are given in Table II.

TABLE II. (Series 18.)

Expt.	λ, μμ.	Initial H_2, mm.	Final H_2, mm.	Slope.	Cell temp.	Expt.	λ, μμ.	Initial H_2, mm.	Final H_2, mm.	Slope.	Cell temp.
97	546	0·1533	0·1270	0·0173	57·0°	101	546	0·0983	0·0815	0·0215	57·3°
98	546	0·1183	0·1127	0·0033	18·3	102	436	0·0821	0·0365	8·80	57·4
99	546	0·1214	0·1072	0·0211	57·0	103	436	0·0340	0·01718	2·97	16·9
100	546	0·0998	0·0916	0·0031	18·0	104	436	0·01760	0·00527	7·48	57·7

Before comparing the slopes at the two room temperatures, it is necessary to correct for the fact that the chlorine concentration at the higher temperature will be less than at the lower temperature, the pressure in both cases being controlled at 45·7 mm., and that therefore the amount of light absorbed will be correspondingly less. On the assumption that the extinction coefficients are independent of temperature, the corresponding factors are 0·89 at 436 μμ and 0·88 at 546 μμ. Taking the intensity exponent n as 0·76, the slopes at 57° in absence of any specific temperature effect become respectively $2·97 \times (0·89)^{0·76}$ and $0·0032 \times (0·88)^{0·76}$. We thus obtain the results in Table III for the higher temperatures. (Expt. 97 is omitted for the reason given above.)

TABLE III.

		Slope.		Temp. coeff. for 10° rise.		
Expt.	λ, μμ.	Calc. in absence of temperature effect.	Found.	Average.	17—27°.	E, kg.-cals.
99, 101	546	0·00290	0·0213	1·667	1·760	9·78
102	436	2·72	8·80	1·335	1·374	5·50
104	,,	,,	7·48	1·282	1·315	4·74

The increased activation required for the reaction at 5461 Å. as compared with that in the continuum is therefore given by Expt. 102 as 4·3 kg.-cals., and by Expt. 104 as 5·0 kg.-cals.

Effect of Wave-length on Quantum Efficiency.—Previous workers in this laboratory investigating this subject had used a form of Bunsen actinometer and electrolytic gas containing traces of oxygen. It was considered advisable to see whether their most striking result, *viz.*, the fall in γ when passing from the visible to the ultra-violet spectrum, could be reproduced when working at low hydrogen pressures, and in absence of both water vapour and oxygen. The technique of following the reaction was as before, inlet tubes for both hydrogen and chlorine being sealed off after the gases had been introduced. The light source was a 200-volt mercury arc, used in conjunction with the large monochromator, the beam from the telescope slit being concentrated on the cell by means of a cylindrical quartz lens. The energy distribution in the radiation was determined by a calibrated thermopile as already described, and the results applied directly when working with all-quartz apparatus. In one series (20), a glass plate was present on the back of the thermopile chamber. In this case, the emergent light was brought to a focus on a calibrated 2-cm. Moll surface thermopile, and the relative intensities of the lines thus compared. In order to concentrate all the issuing light on the thermopile for this purpose, the height of the telescope slit had to be cut down by means of a diaphragm. The relative rates of quantum absorption at any given wave-length and pressure were calculated by combining the above data with the extinction coefficients determined by von Halban and Siedentopf (*Z. physikal. Chem.*, 1922, **103**, 71).

The measurements on which we place most reliance were carried out with 1·7 mm. of chlorine. Under these conditions, the intensity exponent n is 0·97—0·98, and hence the quantum efficiency is almost independent of moderate variations of intensity. We also did measurements with 313 μμ and 436 μμ at 0·11 mm. of chlorine. But in order to obtain comparative results with the weakly absorbed lines at 254 μμ and 546 μμ, it became necessary to work with higher chlorine pressures. Measurements at 45·7 mm. were therefore undertaken. Their interpretation introduced a difficulty, for at such pressures, n is far removed from unity, and consequently, using light beams of widely differing intensity and extinction coefficient, any specific effect on γ of change in λ tends seriously to be masked by the effect due to the changes in rate of quantum absorption. There is really no satisfactory way of overcoming this difficulty. In practice, we determined the slope at 436 μμ by two experiments in which the intensities varied in the ratio of 1 : 1·93. The resulting intensity exponent was found to be 0·69, and this figure,

and also the considerably higher one (0·76) regarded by us, from the general nature of our unpublished data, as normal for these pressures, were both used to correlate the data at different wave-lengths. The results of our three series of experiments are contained in Tables IV—VI, in which r denotes the relative absorbed quanta.

TABLE IV. (Series 20.)

p_{HCl} = 0·5 mm. initially, 1·58 mm. at end; p_{H_2} = 0·62 mm. initially, 0·08 mm. at end; p_{Cl_2} = 1·7 mm. in Expts. 108—117, 0·11 mm. in Expts. 118 and 119.

Expt.	λ, μμ.	Mean slope.	r.	Relative γ.	Expt.	λ, μμ.	Mean slope.	r.	Relative γ.
108	436	0·086	1·00	0·96	114	303	0·064	1·06	0·67
109	405	0·124	1·44	0·96	115	365	1·345	21·0	0·71
110	365	1·12	21·0	0·59	116	436	0·093	1·00	1·03
111	436	0·090	1·00	1·00	117	405	0·115	1·44	0·89
112	313	0·563	9·13	0·69					
113	436	0·095	1·00	1·06	118	313	0·0394	9·71	0·86
					119	436	0·0047	1·00	1·00

Mean relative γ values for Expts. 108—117 : 436 μμ, 1·00; 405 μμ, 0·92; 365 μμ, 0·65; 313 μμ, 0·69; 303 μμ 0·67; for Expts. 118 and 119 : 436 μμ, 1·00; 313 μμ, 0·86.

TABLE V. (Series 21.)

p_{HCl} = 0·0 mm. initially, 0·6 mm. at end; p_{H_2} = 0·538 mm. initially, 0·238 mm. at end; p_{Cl_2} = 1·7 mm. throughout.

120	436	0·0413	1·00	(0·61)	125	436	0·072	1·00	1·06
121	303	0·203	4·27	0·70	126	405	0·101	1·35	1·10
122	436	0·068	1·00	1·00	127	303	0·218	4·27	0·75
123	365	0·870	19·8	0·65	128	265	0·00369	0·0674	0·81
124	313	0·70	15·6	0·66					

Mean relative γ values : 436 μμ, 1·00; 405 μμ 1·07; 365 μμ, 0·63; 313 μμ, 0·64; 303 μμ 0·70; 265 μμ, 0·79.

TABLE VI. (Series 22.)

p_{HCl} = 0·76 mm. initially, 0·95 mm. at end; p_{H_2} = 0·164 mm. initially, 0·067 mm. at end; p_{Cl_2} = 45·7 mm. throughout.

Expt.	γ, μμ.	Mean slope.	r.	$r^{0.69}$.	Relative γ.	$r^{0.76}$.	Relative γ.
129 and 131	436	0·886	1·00	1·00	1·00	1·00	1·00
132	405	1·023	1·14	1·094	1·05	1·105	1·04
133	365	4·58	6·15	3·50	1·48	3·98	1·30
134	313	1·96	2·70	1·985	1·12	2·13	1·04
135	303	0·910	1·05	1·034	0·99	1·038	0·99
136	254	0·0218	0·0121	0·04764	0·52	0·0350	0·70
137	265	0·117	0·0693	0·1586	0·83	0·1315	1·00
139	546	0·0161	0·00268	0·01683	(1·08)	0·01112	(1·63)
140	436	0·810	1·00	1·00	0·91	1·00	0·91

Omitting Expt. 120, for the abnormal result of which we cannot account, and making due allowance for irregularities due to the fact that the 200-volt mercury arc used had to be run off the main supply and not off the Tirrill regulator, there can be little doubt that the figures in Tables IV and V confirm the results obtained in Parts II and III, in that γ falls off very definitely when passing from the visible to the ultra-violet spectrum. Table VI, however, appears to reveal a different state of affairs. In any case, the high values of γ indicated by Expt. 139 for green light are illusory. The conditions of insolation were the same as in Expt. 84 (Table I), and the observed values should be multiplied by about 0·25, which gives 0·3—0·4 as the true relative quantum efficiency. The figures in Expts. 133 and 134 depend on insolation times of 30 and 45 seconds respectively, and for that reason are perhaps not to be regarded as very reliable. These wave-lengths being omitted, it would appear that, if n is taken as 0·69, only the λλ 265 and 254 μμ give the anticipated low values of γ, whilst if 0·76, the " normal " value of n, be taken, then γ seems to be independent of wave-length (omitting the figure for 365 μμ, still abnormally high) from 436 μμ to 265 μμ. The figure for 254 μμ remains low, and the corresponding slope is probably quite sound experimentally; but the relative intensity of this line is particularly subject to fluctuations with changes in the energy input into the lamp. If, on the other hand, apart from Expt. 139, reliance is placed on the relative γ values in col. 6, it may be noted that, qualitatively, they fall in the same order as both the observed

slopes and the relative rates of quantum absorption, increasing from 254 μμ, as wave-length increases, up to a maximum at 356 μμ and then falling off to 436 μμ. This three-fold parallelism is not observed at 1·7 mm. of chlorine.

Our conclusion is that, at low pressures of hydrogen and of chlorine, γ falls off in the ultra-violet region just as was previously found for electrolytic gas containing traces of oxygen, but that, when the chlorine/hydrogen ratio is high, γ is constant down to, at all events, the neighbourhood of 260 μμ. Figs. 1 and 2 summarise graphically the results obtained both in this paper and also in Parts II and III, with the exceptions of our Expts. 118 (discussed later), 120, and 133, as also the value for 405 μμ found in Part II, and attributed (see Part III) to a faulty light filter. In Fig. 1 are collected the results of all measurements with wave-lengths not < 400 μμ, together with the data for higher frequencies contained in Table VI, assuming $n = 0{\cdot}76$; Fig. 2 includes all the data obtained with ultra-violet light which are recorded in Parts II and III and in Tables IV and V. The relative value of γ_{546} given in Part III has been

FIG. 1.

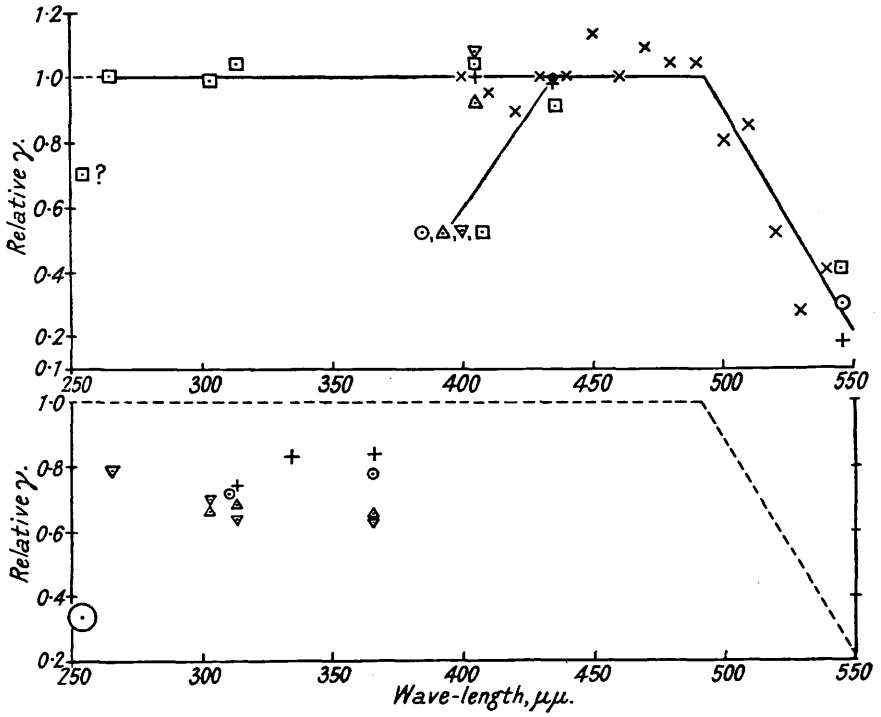

FIG. 2.

multiplied by 0·25, as was done in the case of Expt. 139, and for the same reason. The following notation is employed: Part II, ⊙; Part III, + and ×, for data from mercury-vapour and metal-filament lamp respectively; Table IV, △; Table V, ▽; Table VI, ⊡.

Experiments in Presence of Oxygen.—A few measurements were carried out with about 0·1 mm. oxygen present in the gas, their purpose being to verify the statement of Mrs. Chapman (J., 1923, **123**, 3062) that, at sufficiently low concentrations of hydrogen, oxygen does not act as an inhibitor.

The oxygen was introduced in known amount into the apparatus by heating to dull redness weighed quantities of silver oxide contained in a small side-tube, sealed on to the main apparatus, and separated from it by a tap lubricated with metaphosphoric acid. The whole was thoroughly evacuated, the tap closed, the oxygen liberated in the side-tube, and admitted into the main apparatus, with the chlorine frozen out, after the hydrogen had been added. The volume of the side-tube was negligibly small. The Pirani gauge was first calibrated for oxygen against a McLeod gauge. As $f(v)$ for a gaseous mixture is not the sum of the $f(v)$ values for its constituents (see, *e.g.*, *Proc. Roy. Soc.*, 1928, *A*, **121**, 344; 1932, **134**, 554), a second calibration

was then done, in which the voltage function was determined for various known hydrogen pressures to which 0·1 mm. of oxygen had been added, thus enabling p_{H_2} at any stage of the reaction to be deduced from the $f(v)$ for the hydrogen–oxygen mixture on the assumption that the oxygen pressure remained unaltered. This approximate method, with the necessary corrections for deviations in actual oxygen pressure from 0·1 mm., was considered sufficiently accurate for these experiments. The results are contained in Table VII. The oxygen pressures in the last column were direct measurements after all the hydrogen had been insolated away at the close of the experiment.

TABLE VII. (Series 12 and 13.)

Expt.	p_{Cl_2}, mm.	Initial p_{HCl}, mm.	Initial p_{H_2}, mm.	Final p_{H_2}, mm.	Slope.	r.	Relative γ.	Remarks.
63	1·7	0·72	0·280	0·0619	4·4	0·44	10	Rising slope.
64	13	1·14	0·0619	0·0132	6·7	2·0	3·4	
			0·0132	0·0109	0·24			
65	1·7	3·3	0·133	0·0185	3·4	0·44	7·7	
66	13	3·5	0·393	0·0356	26	8·74	3·0	p_{O_2}, 0·116 mm.
			0·0356	0·0089	2·0			
67	45·7	5·5	0·425	0·0259	13	3	4·3	
68	13·0	0·80	0·452	0·0101	4·6	2·0	2·3	Rising slope.
			0·0101	0·0052	0·56			p_{O_2}, 0·100 mm.
69	13·0	1·7	*ca.* 2	zero				p_{O_2}, 0·099 mm.
70	45·7	5·6	1·2	0·0352	7·7	3	2·6	p_{O_2}, 0·097 mm.
71	166	9·0	0·76	0·101	0·9	3·9	0·24	p_{O_2}, 0·094 mm.
72	166	11·0	154	zero				H_2 added by side-tube; p_{O_2}, 0·076 mm.
73	13	318	0·730	0·0118	1·09	8·7	0·12	p_{O_2}, 0·074 mm.
					0·38	2·0	0·19	HCl determined at end volumetrically after absorption in water.

A comparison between the slopes in Expts. 63 and 65 and those obtained in unpublished work shows 0·1 mm. of oxygen to have no appreciable retarding effect at 1·7 mm. pressure of chlorine. The same holds at 13 mm. of chlorine. Taking n as 0·89 in Expt. 64, the observed slope of 6·7 would become 25 at 8·7 units of absorbed intensity, and this figure and that in Expt. 66 compare well with the average slope of 27 found in absence of oxygen (unpublished). Similarly, the slope found in Expt. 68 (a somewhat uncertain result) agrees reasonably well with that obtained under similar conditions with oxygen-free gas. The results at 45·7 mm. of chlorine, on the other hand, are remarkable. Comparison between Expt. 70 and the corresponding one done in absence of oxygen leads to the conclusion, if both are reliable, that oxygen has markedly accelerated the reaction. Expt. 67 cannot be directly compared with any one done in the absence of oxygen, but its relative γ value is considerably higher than any other observed in our work at this chlorine pressure. Moreover, the results in Series 12, taken as a whole, indicate that, at the same incident intensity, $\gamma_{1\cdot7} > \gamma_{13} < \gamma_{45\cdot7}$, a type of relation not observed in any other of our experiments, although in unpublished work with oxygen-free mixtures we have found instances of $\gamma_{13} < \gamma_{45\cdot7}$. It is very difficult to imagine how oxygen could accelerate the reaction or why it should do so at one particular chlorine pressure. We can therefore offer no explanation for these results, and indeed only quote them because they appear to confirm one another. Expt. 71, at 166 mm. of chlorine, cannot be compared directly with any other done in the absence of oxygen, but there are certain indications, which we need not specify, that the oxygen has had little or no effect. We can therefore conclude from our experiments that, at hydrogen pressures above the order of 0·01 mm., an oxygen pressure of 0·1 mm. exerts no retarding influence.

Two further points remain for consideration. There is some evidence in Expts. 64, 66, and 68 that, at still lower pressures of hydrogen, a marked retarding effect of oxygen enters, the slope falling off to a far greater extent than was found in certain unpublished experiments in absence of oxygen. Moreover, although no retardation at the higher hydrogen pressures was observed, oxygen was consumed in the reaction. These two facts may possibly be connected, for, in order to substantiate the fact that oxygen was used up in an experiment, it was necessary at the end to continue the insolation until all the hydrogen had disappeared. They will be discussed later.

Discussion.

The Reaction at 546·1 μμ.—The experiments in Table I show conclusively that the light of the mercury-green line (546·1 μμ; 18,300 cm.$^{-1}$; 52·0 kg.-cals.) brings about the reaction, a fact which raises points of interest. This line lies in the spectrum region of chlorine absorption characterised by bands which converge at about 478·5 μμ (20,900 cm.$^{-1}$; 59·4 kg.-cals.), a limit marking the threshold of the optical dissociation process $Cl_2(^1\Sigma_g) \longrightarrow Cl\ (^2P_{3/2}) + Cl\ (^2P_{1/2})$, the absorbing chlorine molecule being in its zero vibrational quantum state. The dissociation of the same molecule to two normal ($^2P_{3/2}$) atoms requires 56·8 kg.-cals. (500·0 μμ; 20,000 cm.$^{-1}$). The absorption of a light quantum at 546·1 μμ is therefore, neither directly nor as the result of a subsequent collision, capable of dissociating such a chlorine molecule into its constituent atoms. On the other hand, we have seen that the reaction has a quantum efficiency of about 0·3 of the value in the neighbouring continuum; it therefore involves chains which, in all probability, are of the same atomic mechanism as when initiated by light of shorter wave-length.

A scheme of the type

$$\text{(i)}\ Cl_2 + 52\ \text{kg.-cals.} \longrightarrow Cl_2'$$
$$\text{(ii)}\ Cl_2' + H_2 \longrightarrow 2\ HCl^* + 96\ \text{kg.-cals.}$$
$$\text{(iii)}\ HCl^* + Cl_2 \longrightarrow HCl + Cl + Cl - 56{\cdot}8\ \text{kg.-cals.}$$

is thermochemically possible. But even if the relatively high temperature coefficient of the reaction in this region were to correspond to an extra activation heat of 4—5 kg.-cals. (Table III), making a total energy of 100—101 kg.-cals. available as the result of (ii), it would be necessary to assume that this energy has a high probability of unsymmetrical distribution between the two molecules of hydrogen chloride. More probable might be (i), followed by

$$\text{(iv)}\ Cl_2' + H_2 \longrightarrow HCl + H + Cl.$$

On the assumption just made, this step would be a thermoneutral one, and, for that reason, perhaps plausible. There are, however, at least two objections to such schemes. The relative γ value of about 0·3 at room temperature has been found, not only with gas mixtures containing 0·5 atm. each of hydrogen and of chlorine, but also with a mixture of composition Cl_2 45·7 mm.; H_2 0·1 mm. To bring these results into line with the above suggestion, it would be necessary to assume a very low deactivating efficiency for Cl_2'–Cl_2 collisions, which is unlikely. Further, and applying particularly to the second mechanism, if the high temperature coefficient at 546·1 μμ were due to the necessity of an increased activation of 5 kg.-cals., the relative γ value at room temperature would be far less than 0·3. In fact, and although the matter has not been directly proved experimentally, it is very probable that the high temperature coefficient in question is due, not to any extra activation subsequent to light absorption, but merely to an increase in the extinction of the chlorine, a suggestion first considered in detail by Wulf (*Proc. Nat. Acad. Sci.*, 1930, **16**, 27).

Until recently, there was no evidence to show whether any appreciable part of the very weak absorption in the chlorine banded spectral region was continuous. Jones and Spooner (*Trans. Faraday Soc.*, 1935, **31**, 811) have, however, demonstrated that, at numerous points between 504 and 532 μμ, apparently free from lines, there is very definite absorption, the extinction coefficients being of the same magnitude as those found in the same region by von Halban and Siedentopf (*loc. cit.*), using a method which did not separate the effects of bands and of continuum. Although Jones and Spooner do not exclude the possibility of the presence in these regions of a large number of close unresolved lines, yet it seems likely that the absorption is mainly continuous.* This being the case, and although the measurements in question have not been extended as far as 546·1 μμ, we shall assume that the primary process at this wave-length, and in the banded region generally, is optical dissociation to chlorine atoms, the absorbing chlorine molecules being of course

* We are much indebted to Dr. A. Elliott, of the University of Sheffield, for having kindly initiated these experiments.

in higher vibrating levels of the normal state. The difference, ΔE, of 4·3—5·0 kg.-cals. between the activation energies at 436 μμ and 546 μμ, as calculated from the respective temperature coefficients, is due to an "activation energy" of the absorption process, and corresponds to the average energy difference between the actual absorbing molecules and those in the lowest vibrational quantum state. The differences in level between these higher states and $v'' < 0$ are as follows :

v''	1	2	3	4	5
Wave-number, cm.$^{-1}$	557	1106	1647	2180	2706
Kg.-cals.	1·58	3·14	4·68	6·19	7·69

The found value for ΔE suggests, therefore, that the absorbing molecules are those in which v'' is either 3 or 4, and chiefly the former. It is plain that in neither case will the energy content of these molecules, after absorption at 546·1 μμ, permit of dissociation into $^2P_{1/2}$ and $^2P_{3/2}$ atoms (59·4 kg.-cals.). But clearly, all such molecules with $v'' = 4$, as also molecules with $v'' = 3$, assuming a slight contribution of 0·1—0·2 kg.-cals. of rotational energy, are potentially capable of giving two $^2P_{3/2}$ atoms (56·8 kg.-cals.).

According to Mulliken (*Physical Rev.*, 1930, **36**, 1440), chlorine, as also the other halogens, in addition to its known O_u^+ upper state, should also have three other associated upper states, components of a $^3\Pi$ multiplet, all with small D values (one of them repulsive), converging to a limit at 20,000 cm.$^{-1}$, and hence dissociating into two $^2P_{3/2}$ atoms. In the case of iodine, the infra-red band absorption system discovered by Brown (*ibid.*, 1931, **38**, 1187) is very possibly associated with transition from the normal state to one of these upper states, and a similar direct transition into the continuum of one of these states may perhaps be taking place in the case we are considering, with the result that chlorine atoms will be produced by absorption at 546·1 μμ. In addition, however, an excited molecule in the O_u^+ state will have a certain probability of transition, by a predissociation process, into one of these $^3\Pi_u$ states, and this is the interpretation of our results which we prefer (cf., for iodine, van Vleck, *ibid.*, 1932, **40**, 544). A mechanism of this sort appears preferable to one involving collision between excited chlorine and other molecules. If the latter were correct, the relative γ value for 546 μμ should decrease rapidly when the total pressure is lowered below a certain low limit. It would be very difficult to test this point experimentally. We found γ to be much the same at $p = 47$ mm. as at $p = 1$ atm., *viz.*, 0·3. Presumably this figure measures the probability of the $O_u^+ \longrightarrow {}^3\Pi_u$ transition referred to. Less likely possibilities are that it depends on the probability that the absorption of 546·1 μμ light will raise normal chlorine molecules with $v'' = 3$ to the energy level of 56·8 kg.-cals., or that it depends on a difference of reactivity towards hydrogen molecules of excited and normal chlorine atoms.

It will have been noted that the agreement between Expts. 102 and 104 (Table III) is defective. On the basis of the above discussion, and on the assumption that Expts. 98—101 are sound, the result given by Expt. 104 is to be preferred, although a value of E_{436} of 5·0 kg.-cals. (temp. coeff. for 17—27° = 1·336) would be in conformity with the suggestions put forward; E is, of course, a composite figure, corresponding to the complex nature of the reaction under study.

Wave-length and Quantum Sensitivity.—The data from Part III plotted in Figs. 1 and 2 show that, as the wave-length of the exciting light decreases from 546·1 μμ, γ (relative) increases and reaches unity at about 490 μμ, a point still inside the banded spectrum region, but corresponding to 58·0 kg.-cals. per mol., a value sufficient to dissociate the absorbing molecule into two normal atoms. The steady rise of quantum efficiency we interpret as due to an increasing probability of spontaneous formation of two $^2P_{3/2}$ atoms from the excited O_u^+ state. We should expect to find a progressive decrease in temperature coefficient in the same region. In the temperature range 27—45°, Hertel (*Z. physikal. Chem.*, 1932, *B*, **15**, 325) found 1·48 for 480—515 μμ, as compared with 1·37 for 400—480 μμ. The value of ΔE derived from these figures, about 1·50 kg.-cals., is rather less than that corresponding to $v'' = 1$, *viz.*, 1·58 kg.-cals.; these molecules in turn would require to absorb at 515 μμ in order that they might be raised to the level of 56·8 kg.-cals./mol.

Further inspection of Figs. 1 and 2 shows γ (relative) to remain constant within experi-

mental error, at all events as far as 400 μμ. Below this wave-length, values are only available for light of the mercury lines at 366, 334, 313, 303, 265, and 254 μμ, the gap between 400 and 366 μμ being particularly unfortunate. The diagrams show, however, that although, with oxygen-free gases and a chlorine pressure of 45·7 mm., the quantum efficiency is not affected, or only doubtfully so (see discussion following Table VI), by increase in frequency over this wave-length range, yet it falls off appreciably in the two cases of (i) $p_{Cl_2} = p_{H_2} = 0{\cdot}5$ atm., oxygen present; and (ii) $p_{Cl_2} = 1{\cdot}7$ mm., $p_{H_2} = 0{\cdot}2$ mm., oxygen absent; the average value of γ (relative) being less than 0·8 and 0·7 respectively. In the latter case, a single comparison using $p_{Cl_2} = 0{\cdot}11$ mm. gave $\gamma_{313} = 0{\cdot}86$, whereas it was 0·65 at $p_{Cl_2} = 1{\cdot}7$ mm.

A change in frequency in the continuous-spectrum region can only affect the properties of the primary products of reaction, *i.e.*, the chlorine atoms. The higher the frequency, the greater will be their relative kinetic energies at the moment of separation. There is every reason to suppose that the reaction probability between colliding chlorine atoms and hydrogen molecules will be greater, rather than less, the higher their relative kinetic energy of approach. Nor will the course of the normal reaction chain depend appreciably, one way or the other, on the high velocity of the chlorine atom which initiates it. The only way in which the high frequency of the light can shorten the chain length appears to be by providing the activation energy required for the production of some substance, the formation of which reduces the concentration of the chain carriers (hydrogen or chlorine atoms) in the reacting system. After considering various possibilities, we put forward the following suggestions. The wave-lengths 478·5, 400, and 366 μμ correspond respectively to absorbed energy quantities of 59·4, 69·4, and 77·6 kg.-cals./mol. The average molar kinetic energies of separation of chlorine atoms produced at 400 μμ will be then 5 kg.-cals., and at 366 μμ, 9·1 kg.-cals. The activation energy of the assumed process will lie between these limits.

We think that in the case of the experiments with 1·7 mm. of chlorine and low pressures of hydrogen set out in Tables IV and V, the effect observed is due to the reaction $Cl + Cl_2 \longrightarrow Cl_3$, taking place when the collision involves a chlorine atom of sufficiently high kinetic energy. The conditions of formation of Cl_3 radicals have recently been studied theoretically by Rollefson and Eyring (*J. Amer. Chem. Soc.*, 1932, **54**, 170). They conclude that the above reaction requires an activation energy with maximum and most probable values of 8·6 and 4·5 kg.-cals./mol. respectively, that this activation energy is entirely translational in nature, and that the quasi-molecule Cl_3' (the reaction $Cl + Cl_2 \longrightarrow Cl_3$ is probably exothermic), when once produced, will have a relatively long life, the above equation expressing this fact by not postulating the necessity of a three-body collision. As the ratio p_{H_2}/p_{Cl_2} in the present case is of the order of 0·1, it follows that, with light of sufficiently short wave-length, the result of the primary reaction is, to a great extent, the formation of two Cl_3 radicals rather than two Cl atoms. In these experiments, moreover, the chains are almost entirely broken on the walls (adsorption of chlorine atoms and recombination to molecular chlorine). A consideration of our quantum yields at the lowest pressure used, combined with calculations of collision numbers and of rates of diffusion of chlorine atoms to the walls of the reaction vessel, shows (details in a subsequent paper) that the efficiency of the latter in removing chlorine atoms from the reaction zone is very low, in agreement with the observations of Rodebush and Klingelhoefer (*J. Amer. Chem. Soc.*, 1933, **55**, 130) and of Schwab and Friess (*Z. Elektrochem.*, 1933, **39**, 586). It is natural to suppose that Cl_3 radicals are adsorbed more readily than Cl atoms and, as in these experiments they will have been present in concentrations far above the equilibrium value, a shorter chain length will be the result. Combined with this is the further fact that the efficiency of Cl_3–H_2 collisions is very probably less than that of Cl–H_2 collisions. According to Kimball and Eyring (*J. Amer. Chem. Soc.*, 1932, **54**, 3876), this ratio is as low as 10^{-3}—10^{-4}, whereas Rollefson (*J. Amer. Chem. Soc*, 1934, **56**, 579) puts it at 10^{-1}—10^{-2}. In any case, under the low pressure conditions prevailing in the experiments under discussion, even the latter disparity would be of importance, and the combination of the two factors we believe fully adequate to explain our results. The smaller effect found at $p_{Cl_2} = 0{\cdot}11$ mm. is to be anticipated in view of the larger proportion of photo-dissoci-

ated chlorine atoms which undergo their first collision after formation with hydrogen rather than with chlorine molecules.

The above interpretation of the experiments assumes a higher ratio $[Cl_3]/[Cl]$ than corresponds to the equilibrium $Cl_2 + Cl \leftrightarrow Cl_3$. The higher the total pressure, the more rapidly will equilibrium conditions be set up by molecular collisions, and the less important will be the rôle of the walls in terminating chains; consequently, the less likely will be any effect of wave-length on quantum efficiency. This we believe to be the reason for the difference between the results in Table VI as compared with those in Tables IV and V. Light of short wave-length will, as before, result in the formation of Cl_3 radicals, but for the reasons just given there will be no measurable effect on the quantum efficiency.

From what has been said, the proposed mechanism clearly cannot be responsible for the effects found with electrolytic gas at atmospheric pressure. This gas contains oxygen, and we suggest tentatively that the processes responsible for the decreased value of γ in short wave-length light (a rather smaller decrease than that just discussed) may be reactions of the type $Cl' + O_2 \longrightarrow ClO_2$, $Cl_3' + O_2 \longrightarrow Cl_2 + ClO_2$, the high translational energy of primarily formed chlorine atoms again supplying the necessary activation. The powerful inhibiting effect of ClO_2, most probably by the way of $ClO_2 + H \longrightarrow HCl + O_2$, is of course well known. Further examination of this suggestion reveals difficulties. Quite apart from questions of magnitude and nature of activation energy, the absolute quantum efficiencies measured in Part III are believed to have been only one-tenth of those obtained in Part II, respectively of the order of 10^4 and 10^5. The main chain-breaking reaction in both cases was the same ($H + H_2 + O_2 \longrightarrow$ products), indicating that the oxygen pressure was about ten times as high in the former as in the latter experiments. But the relative lowering of γ brought about by ultra-violet light was about the same in both cases. It is of course possible, but not very likely, that the estimate of absolute quantum efficiency in Part II (filtered light used) was seriously in error. We are not now in a position to test this point, and in the circumstances will not discuss the matter further, beyond remarking that calculations indicate that, if the reaction $Cl' + O_2 \longrightarrow ClO_2$ is solely responsible for the effect, the Cl' atom must still be capable of reacting in this sense after at least 30 collisions with other molecules in the gaseous mixture. If $Cl_3 + O_2 \longrightarrow Cl_2 + ClO_2$ is responsible (the reaction would probably have a slight positive heat effect), then the conditions are, quite generally, more favourable to the suggestion.

Experiments in Presence of Oxygen.—We have left for discussion two points. The first is that, although 0·1 mm. of oxygen does not retard the reaction if the hydrogen pressure is of the order of 0·1 mm., yet a very marked retardation is observed at hydrogen pressures of the order of 0·01 mm. Although the accurate determination of small hydrogen pressures in presence of excess of oxygen is liable to appreciable error, we nevertheless think the effect a real one. The second point is that although at the higher pressures of hydrogen mentioned, oxygen does not retard reaction, yet some of it is found to have disappeared when, after the end of the experiment, all hydrogen present has been insolated away. It is of course possible that this oxygen consumption merely took place during the last stages of this final insolation, *i.e.*, when p_{H_2} had fallen to less than 0·01 mm., and the oxygen retardation referred to above had set in. Assuming, however, oxygen to have been consumed over the whole of our pressure range, we suggest the following explanation:

The primary process at all pressures of hydrogen is the union of hydrogen atoms and oxygen molecules:

$$(a)\quad H + O_2 \longrightarrow HO_2 + 40 \text{ kg.-cals.}$$

Reaction between this radical and hydrogen molecules can be conceived of as taking place in two ways, *viz.*,

$$(b)\quad HO_2 + H_2 \longrightarrow H_2O + OH + 63 \text{ kg.-cals.}$$
$$(c)\quad HO_2 + H_2 \longrightarrow H_2O_2 + H - 2 \text{ kg.-cals.}$$

Although (*b*) is highly exothermic, we suggest that it will at ordinary temperatures take place much less readily than (*c*), owing to its higher activation energy. This results

from the necessity of breaking both an O–O and an H–H linkage, whereas in (*c*) the latter only must be broken. On the other hand, it will take place more readily than (*c*), owing to its greater exothermicity, when H–O_2–H_2 triple collisions occur, the result of such collisions being

$$(d)\quad H + O_2 + H_2 \longrightarrow H_2O + OH + 103 \text{ kg.-cals.}$$

Both Chapman and Watkins (J., 1933, 743) and Norrish and Ritchie (*Proc. Roy. Soc.*, 1933, *A*, **140**, 713) ascribe the retarding effect of oxygen at high hydrogen pressures to reaction (*d*), and in all probability it was responsible for the large consumption of oxygen in our Expt. 72 (Cl_2 = 166 mm.; initial H_2 = 154 mm.).

At the lower hydrogen pressures used in our other experiments, triple collisions became very rare events. Such reactions as

$$HO_2 + Cl_2 \longrightarrow OH + Cl_2O - 15 \text{ kg.-cals.}$$
$$HO_2 + Cl_2 \longrightarrow HClO + ClO - 8{\cdot}5 \text{ kg.-cals.}$$
$$HO_2 + HCl \longrightarrow H_2O + ClO + 7{\cdot}5 \text{ kg.-cals.}$$

we imagine to be excluded in practice; apart from the endothermicity of the first two, all would have high activation energies. The HO_2 radicals will rather react in accordance with (*c*); and this reaction, with the regeneration of a hydrogen atom, will correspond to our observations, *i.e.*, consumption of oxygen without inhibition of hydrogen chloride formation. Finally, as the hydrogen pressure falls still further, reaction (*c*) will become unimportant compared with (*e*) $HO_2 \longrightarrow H_2O_2$, H_2O, O_2, occurring either on the walls or in the gas phase, and consumption of oxygen will again be accompanied by retardation of the main reaction.

In the absence of more experiments, we shall not discuss the above suggestions any further, beyond mentioning that they may be relevant in connexion with the somewhat discordant experimental results obtained during the study of the photochemistry of hydrogen–oxygen mixtures (Hinshelwood and Williamson, "Reaction between Hydrogen and Oxygen," Chapter III, 1934). They would point to low total pressures and temperatures as favouring the formation of hydrogen peroxide, and high total pressures and temperatures that of water.

SUMMARY.

(1) Experiments with carefully monochromatised light confirm the earlier conclusion that a hydrogen–chlorine mixture will react in light of wave-length 546 μμ. On the other hand, negative results were obtained at 579 μμ.

(2) Comparative measurements of the temperature coefficient of the reaction at 436 μμ and 546 μμ have been carried out.

(3) In gas mixtures free from oxygen and of about 2 mm. total pressure, the relative quantum efficiency is found to be lower in ultra-violet than in visible light. At higher pressures no such difference was observed.

(4) At hydrogen pressures of 0·01—0·5 mm., the presence of 0·1 mm. of oxygen does not retard the reaction although oxygen appears to be consumed. Evidence was obtained of a marked retardation when the hydrogen pressure fell below 0·01 mm.

(5) The above results are discussed and explanations proposed. In connexion with (1) and (2), it is suggested that active light absorption in the green is connected with the continuous background of the banded spectrum region, and that the reaction mechanism is essentially the same as when absorption takes place in the continuum proper. The observations under (3) are explained on the basis of a mechanism involving the formation of Cl_3 radicals in light of short wave-length.

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