41. *The Photochemical Union of Hydrogen and Chlorine. Part III. The Effect of Wave-length on Quantum Efficiency. Experiments with Dispersed Light.*

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IN Part II (J., 1930, 2709), Allmand and Beesley described experiments which led them to the conclusions (i) that the quantum yield of the reaction reaches a maximum in the violet, and falls off at both longer and shorter wave-lengths, particularly at the latter, and (ii) that the reaction is definitely sensitive to light of wave-length 546 μμ (the mercury green line). In the present paper we describe experiments which were made during the two sessions 1928—1930 with the purpose of confirming or otherwise these rather unexpected results. As the consequence of an unfortunate, then unsuspected, defect in the monochromator used, the data obtained in the ultra-violet region were very misleading and, even after correction, are not as conclusive in detail as we could wish. Their discussion on this account will be curtailed.

Work on this subject up to 1930 is summarised at the commencement of Part II. Since then, further papers have appeared. Hertel (*Z. physikal. Chem.*, *B*, 1931, **14**, 443) finds the quantum yield in the banded spectrum region at 480—515 μμ to be about one-seventh of that in the neighbouring continuum below 478·5 μμ; Norrish and Ritchie (*Proc. Roy. Soc.*, *A*, 1933, **140**, 713) find $\gamma_{365} : \gamma_{406}$ to be 1·06 (mean of five concordant results) for gaseous mixtures rich in oxygen; and Professor Bodenstein has informed us that experiments in his laboratory show the quantum yield to be independent of wave-length between 250 and 500 μμ.

EXPERIMENTAL.

Apart from the method of insolation, the apparatus and methods used were very similar to those employed by Allmand and Beesley (Part I, J., 1930, 2694), and only points of difference will be noted. The electrolytic gas generator electrodes were sealed in by means of a special cement, made by chlorinating naphthalene in presence of antimony trichloride, and subsequently extracting the product with hydrochloric acid and with distilled water. Three bubblers in series, instead of one, were interposed between generator and reaction vessel. The latter was the identical quartz cell used by Allmand and Beesley, but (i) provided with an additional entry for gas so arranged that, by turning a three-way tap, mercury-sealed and water-lubricated, the electrolytic gas could be either bubbled through the water layer on the bottom of the cell, or allowed to enter the cell above this level; (ii) connected with the glass parts of the apparatus by graded quartz–soda glass unions instead of mercury-sealed ground joints; (iii) completely immersed in a copper thermostat provided with a quartz window, and suspended rigidly in position from an optical bench mounted above the thermostat. The latter was provided with a brass extension, into which was fixed a long horizontal glass tube about 3 cm. in diameter. The capillary indicating tube of the actinometer, of about 2 mm. bore and 6 feet in length, was housed inside this tube, which also contained a 2-metre silvered-brass scale, graduated in mm., and clipped rigidly on to the capillary. Water was circulated through the thermostat and its extension by means of a pump, designed by Mr. H. N. Ridyard and provided with a mercury seal which effectually prevented any contamination of the thermostat water with oil from the pump bearings. There was no appreciable difference at any time between the temperature of the main thermostat and of the extension housing the actinometer capillary.

Insolation was effected by either a quartz–mercury lamp (usually over-run at 4·6 amps. and 60 volts) or a 2000 c.p. tungsten-filament lamp, in conjunction with a large-aperture quartz monochromator already described elsewhere (F. J. Perry, *Trans. Optical Soc.*, **1932**, **33**, 159). The energy of any particular wave-length leaving the telescope slit was measured by means of a vacuum linear thermopile mounted behind the slit, a vernier potentiometer reading to 10^{-8} volt being used in the earlier work, and direct deflexions on a Broca galvanometer being employed later. The beam passing through the plate at the rear of the thermopile chamber was strongly divergent, and was caused to traverse the thermostat window and cell by means of a pair of quartz lenses.

In all cases, the relative amounts of absorbed energy were calculated from the thermopile readings (corrected for selective absorption in the vitreous silica end of the reaction vessel) and the known extinction coefficients of chlorine, as the lenses then available did not enable us to collect the whole of the beam on to a thermopile placed behind the cell. This method of work was the immediate cause of the erroneous conclusions originally (see *Trans. Faraday Soc.*, **1931**, **27**, 426) drawn with regard to the behaviour of the reaction mixture towards ultra-violet light; for the exit-window of the thermopile chamber, through which the light beam necessarily passed before entering the reaction vessel, was eventually found to consist of glass and not of quartz (see *Nature*, **1933**, **131**, 656). The result, of course, was that we observed no detectable reaction with light supposed to be of wave-lengths 254, 265, and 280 $\mu\mu$, and less reaction to varying degrees than corresponded to the true state of affairs between 289 and 334 $\mu\mu$. The transmission of the glass plate has since then been determined photographically down to 280—284 $\mu\mu$, where it becomes negligible, and these figures have enabled us to make use, to some extent, of our data. Unfortunately, the relatively large error in measurement involved by working with such small actual intensities cannot be compensated for in this way.

In two or three respects, the results as a whole, experimentally considered, differed from those obtained by Allmand and Beesley. The changes in gas sensitivity during an experiment (*loc. cit.*, p. 2702) were distinctly less marked in our case. This fact is very probably connected with another, *viz.*, that our absolute values of quantum sensitivity were lower. Whereas they, in their definitive experiments, invariably had efficiencies of the order of 10^5, only with our most sensitive gas mixtures did we reach this figure, and most of our measurements gave values of the order of 10^3—10^4. Our gases presumably contained more oxygen, and this may perhaps be connected with the fact that we did not employ the device of a slowly alternating current (*loc. cit.*, p. 2695) in our gas generator. With our most sensitive gas mixtures, we noticed variations in sensitivity during an experiment, just as did Allmand and Beesley.

On the other hand, all through our work we never succeeded in eliminating with certainty a slight degree of " drift " in the actinometer tube, *i.e.*, the water meniscus tended to move slowly when the gas stream was cut off prior to illumination. This was traced to the taps (mercury-sealed and water-lubricated) between the generator and the photochemical cell (and partly remedied), and there is no doubt that some form of magnetically operated internal glass seal would have been an improvement. Needless to say, no measurements have been utilised in which " drift " was of any importance. There was never any trace of an induction period, and the Draper effect was always marked.

As our standard of comparison, and when working with the quartz–mercury lamp, the reaction at 405 $\mu\mu$ was taken. A set of measurements involved successively (*a*) drift reading if any, (*b*) reaction at 405 $\mu\mu$, (*c*) drift, (*d*) reaction at λ, (*e*) drift, (*f*) reaction at 405 $\mu\mu$, (*g*) drift. If the apparatus were free from drift at the time, (*a*), (*c*), (*e*), and (*g*) were omitted. Energy (thermopile) readings were taken at convenient moments—if possible, during the intervals (*c*) and (*e*), and nearly always during (*a*) and (*g*), *i.e.*, immediately before and immediately after a series of readings. Close agreement was generally obtained. When using the metal filament lamp, the procedure was identical, except that the reaction at 430 μμ was taken as the standard of comparison.

The calculation of the results has followed on normal lines; 4% of the light transmitted by the chlorine is assumed to have been reflected back from the end plate into the gaseous mixture. The transmission of the empty reaction vessel has been measured between 254 and 436 μμ. It varies with wave-length to an appreciably greater extent than would correspond to differences in reflexion losses. This is presumably due to selective absorption by the vitreous silica end-plates, and the corresponding correction—a small one—has been applied. Its effect and that of the glass plate correction are shown separately in the relevant table.

Results.

Effect of Intensity with 313 μμ *Light.*—Allmand and Beesley had investigated the effect of intensity with monochromatic light of wave-lengths 405 μμ and 436 μμ, and had shown that, over measured intensity ranges of 180 : 1 and 440 : 1 respectively, velocity and intensity were practically proportional under their experimental conditions. We thought it desirable to test the matter with ultra-violet light. Experiments were accordingly done in which the intensity at 313 μμ was varied by putting in front of the collimator slit of the monochromator (*a*) a liquid filter consisting of layers of aqueous potassium chromate and of *p*-nitrosodimethylamine, (*b*) a Noviol glass filter (G. 585), (*c*) both filters together. The results were as follows, comparison being made with the velocity and intensity obtained with the unweakened light.

Filter.	Relative intensity.	Relative velocity.	Velocity/intensity.	
(*a*)	0·452	0·484	1·071	Mean 1·022
	0·463	0·484	1·045	
(*b*)	0·298	0·276	0·926	
(*c*)	0·128	0·134	1·047	

Effect of Wave-length on Quantum Sensitivity.—(i) *Results with mercury vapour lamp.* Measurements were made at the following wave-lengths—254, 265, 280, 289, 303, 313, 334, 366, 405, 436, 492, and 546 μμ. No reaction was observed with the first three lines, for the reason already given. A very slight but definite effect was found with 289 μμ; it will be referred to later. For other reasons, the results at 492 and 546 μμ will also be treated separately. Table I contains the data for 303—436 μμ, referred to 405 μμ as unity. Cols. 2—7 contain, respectively, the number of comparisons actually made; the average ratio of the observed meniscus velocities for 405 μμ and the wave-length concerned; the mean values of the relative quantum sensitivities without any correction; the fractional transmissions of the vitreous silica end-plate; the fractional transmissions of the glass plate; the corrected relative quantum efficiencies. Col. 4 also shows (i) the average deviation of the separate figures from the mean value and (ii) the most probable error of the mean value. Similar figures are contained in col. 7.

TABLE I.

1.	2.	3.	4.	5.	6.	7.
303 μμ	3	15	0·25 (± 0·11) (± 0·06)	0·81	0·25	0·96 (± 0·42) (± 0·23)
313	7	2·3	0·36 (± 0·06) (± 0·02)	0·82	0·46	0·74 (± 0·12) (± 0·04)
334	4	14	0·71 (± 0·04) (± 0·02)	0·84	0·79	0·83 (± 0·05) (± 0·02)
366	11	0·6	0·82 (± 0·11) (± 0·03)	0·86	0·88	0·84 (± 0·11) (± 0·03)
405			1·00	0·87	0·89	1·00
436	10	0·9	0·99 (± 0·045) (± 0·012)	0·88	0·89	0·98 (± 0·045) (± 0·012)

One further result may be mentioned. A single direct comparison was made in an early experiment between 313 and 366 μμ, and an uncorrected value of 0·49 obtained for $\gamma_{313} : \gamma_{366}$. Application of the above corrections gives a ratio of 0·98, about 10% higher than that corresponding to Table I.

There is no doubt that any effect of wave-length on quantum yield in this region is far smaller than was originally thought. This is confirmed by the result of the comparison between

289 μμ and 405 μμ referred to above. This experiment was carried out under very favourable conditions (complete absence of " drift ") and the reaction in the weak 289 μμ light, although very small (0·9 cm. in 131 minutes), was unmistakable. The uncorrected relative value of γ was about 0·05, which becomes 1·6 when corrected. The possible error in estimating the fraction of 289 μμ light passed by the glass plate is very large (we have taken the transmission as 3%) and that in estimating the velocity considerable; one can only conclude that γ is of the same order as at longer wave-lengths.

The probable error in the figure given for 303 μμ (Table I) is also seen to be very high, and this raises the question as to whether the apparently definite fall off in quantum efficiency indicated in the table when passing from the visible to the ultra-violet region is real. It is true that the correction applied at 313 μμ is uncertain, the transmission–wave-length curve for the glass plate being very steep in this region. On the other hand, this does not apply at 334 or at 366 μμ, and we find it difficult to interpret our experiments otherwise than in the obvious sense indicated by the results. It may be added that, whilst we are quite unable to confirm the marked maximum value of γ found by Allmand and Beesley at 405 μμ, and can only assume some serious error in the filter used by them, their relative figures for 313, 366 and 436 μμ (*viz.*, 1·00 : 1·08 : 1·41 : : 0·74 : 0·80 : 1·04) are similar to ours, *viz.* 0·74 : 0·84 : 0·98.

The experiments at 492 μμ presented a special interest, inasmuch as the wave-length lies just beyond the convergence limit of the chlorine banded spectrum (478·5 μμ). A perfectly definite reaction was found with sensitive gas mixtures. Experiments using a Noviol glass filter (38 H; transmission 0·00 at 436 μμ; 0·57 at 492 μμ; 0·80 at 546 μμ) showed that, if this reaction were due to stray 405 or 436 μμ light, the latter would necessarily form an impossibly high proportion of the total radiation issuing from the telescope slit adjusted to 492 μμ. This was confirmed later, when the latter was photographed by means of a small Hilger quartz spectrograph. The amount of stray light was found to be exceedingly small, certainly not more than 0·25% of the total radiation in the beam.

Quantitatively, the results were surprising. Making full allowance for the small amount of " drift," and working with gases of very constant sensitivity (as shown by the uniform reaction rates in 405 μμ), the relative quantum efficiencies were found to be low initially, certainly less than unity compared with 405 μμ (figures of 0·59, 0·69, 0·68, and 0·26 were observed, the last with a very low incident intensity). Then, however, they progressively increased, finally reaching values in the region of 8, which remained remarkably constant over long periods of insolation. If, whilst these values were still rising, the light were cut off for an interval, they were found to have fallen somewhat on re-illumination; but when the maximum figure had been reached, dark periods had no such effect. We emphasise the fact that the figures quoted are *relative* values; the observed velocities in 405 μμ remained constant, or practically so. As mentioned above, the gases were highly sensitive. The maximum observed velocities in 492 μμ were only about 2% of those found in 405 μμ; the lowest velocities, corresponding to what might be imagined to be a normal quantum sensitivity ratio, were of the order of 0·1%. These observations were made towards the end of the work, and we were unable to follow them up at the time. Qualitatively, some kind of resonance action might perhaps be expected in this region (cf. Mecke, *Trans. Faraday Soc.*, 1931, **27**, 369), but the magnitude of the effect is quite inexplicable.

With 546 μμ, using high intensities and sensitive gas mixtures, a perfectly definite reaction was also obtained. This was also the case when using, in addition, either of two Noviol glass filters, with respective transmissions: (i) 579 μμ 0·90; 546 μμ 0·89; 436 μμ 0·02; 405 μμ 0·00, and (ii) 546 μμ 0·79; 492 μμ 0·59; 436 μμ 0·00. The actual velocities observed with this ray were about 0·1% of those given by 405 μμ. The relative quantum efficiencies were between 0·53 and 0·81, the mean figure being 0·70. There was some slight evidence of a rise in this ratio during the course of an experiment, but such an effect, if present, was far less pronounced than with 492 μμ.

(ii) *Results with a continuous light source.* In these measurements, the light energy from the telescope slit is, of course, not strictly monochromatic and, at any given setting of the monochromator, the energy distribution across the slit will depend on the wave-length range embraced by it and by the image of the collimator slit, as also on the energy distribution in the light source. The somewhat complex calculations necessary, unsuitable for reproduction here, will be omitted. With the larger pair of slit widths employed in the first series of measurements (collimator 0·075 cm., telescope 0·0254 cm.), the wave-length range embraced by the issuing light varied from 12·4 μμ at 400 μμ, through 15·7 μμ at 430 μμ, to 30·6 μμ at 540 μμ. In the second series of measurements, collimator and telescope slit widths were both halved, with a corresponding increase in the monochromatism of the light employed, accompanied by a halving of its intensity. The wave-length settings employed ranged between 400 and 540 $\mu\mu$. Some measurements were carried out down as far as 350 $\mu\mu$, but, in consequence of low intensities and velocities, neither of which could be accurately measured, they are not included. Qualitatively, they point to a decrease in γ as frequency increases, and, to this extent, are in agreement with the data in Table I. A single experiment at 550 $\mu\mu$ gave definite evidence of reaction, but disturbance during the measurements made it impossible to calculate the relative quantum efficiency. The results, referred to 430 $\mu\mu$ as unity, are contained in Table II.

TABLE II.

Setting of monochromator, $\mu\mu$.	Series 1.	Series 2.	Mean.	Setting of monochromator, $\mu\mu$.	Series 1.	Series 2.	Mean.
400	—	1·01	1·01	480	1·14; 1·11	0·86	1·04
410	—	0·95	0·95	490	1·13; 1·28; 1·00	0·75	1·04
420	—	0·89	0·89	500	0·88; 0·89; 0·71	0·72	0·80
430	1·00	1·00	1·00	510	0·71; 0·96	—	0·83
440	1·03; 0·99	0·97	1·00	520	0·72; 0·46; 0·38	—	0·52
450	1·07; 1·13; 1·09	1·22	1·13	530	0·46; 0·10	—	0·28
460	1·03	0·98	1·00	540	0·41	—	0·41
470	1·04; 1·15	—	1·09				

Except for the absence of any anomalous effect in the region of 490 $\mu\mu$, these results in general confirm those obtained with the mercury lamp in the same wave-length region. In particular, it would seem (i) that γ is independent of λ over the range 400—500 $\mu\mu$, and (ii) that light in the region of the 546 $\mu\mu$ mercury line is definitely active, but with a reduced efficiency. Discussion of these results, as of those in the earlier sections of the paper, will be postponed, pending the publication of other completed data, obtained by a different technique.

SUMMARY.

Under the prevailing experimental conditions:

(1) The rate of photochemical union of hydrogen and chlorine in monochromatic light of wave-length 313 $\mu\mu$ was proportional to the intensity.

(2) The quantum yield was independent of wave-length between 400 and 490 $\mu\mu$.

(3) The quantum yield was of the same order as in (2) between 400 and 290 $\mu\mu$; it appeared to fall off by 10—20% when passing from the visible to the ultra-violet region.

(4) The quantum yield gradually fell off when passing from 490 $\mu\mu$ to longer wave-lengths. A definite reaction was found in the region of 540—550 $\mu\mu$.

(5) Anomalous observations were made when using monochromatic mercury lamp radiation of 492 $\mu\mu$.

The above work was carried out during 1928—1930. One of us (J. B. B.) hereby acknowledges a maintenance grant received from the Department of Scientific and Industrial Research. Both authors are indebted to Imperial Chemical Industries Ltd. for grants from which the large monochromator and several pieces of auxiliary apparatus were purchased. They also gratefully acknowledge the help received in various ways from Messrs. E. P. Davey, R. C. Johnson, H. N. Ridyard, and D. W. G. Style.

KING'S COLLEGE, LONDON. [*Received, December 5th*, 1933.]