LXXXII.—*The Photolysis of Aqueous Hydrogen Peroxide Solutions. Part II. Experimental Results.*

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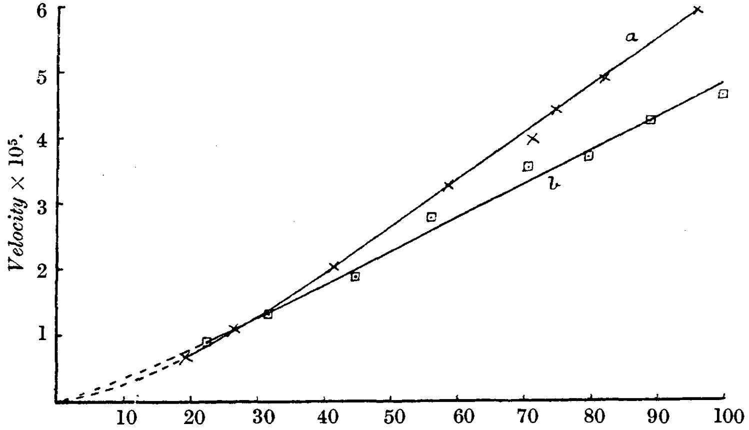
A. *Experiments with Merck's Perhydrol.*

Effect of Intensity and of Intermittent Illumination.—These measurements were all carried out on undiluted perhydrol (about 10*M*). Curve *a*, Fig. 1, shows the results of true intensity variation with a beam of 365 μμ light. Intensity is expressed as cals./cm.^{2}/sec., and velocity as g.-mols. decomposed per hour. The total area irradiated at the front of the cell was 5·6 cm.^{2}, and the time of reaction was 1—3 hours. Above a certain minimum intensity, the velocity is seen to be proportional to $I_0^{0·5}$. This unexpected result led us to undertake measurements in which the average intensity was altered by varying the aperture of a rapidly rotating sector between the limits of 5 and 100% of its full value. The data obtained, shown in Curve *b*, Fig. 1, are seen to be of the same general nature as with true variation.

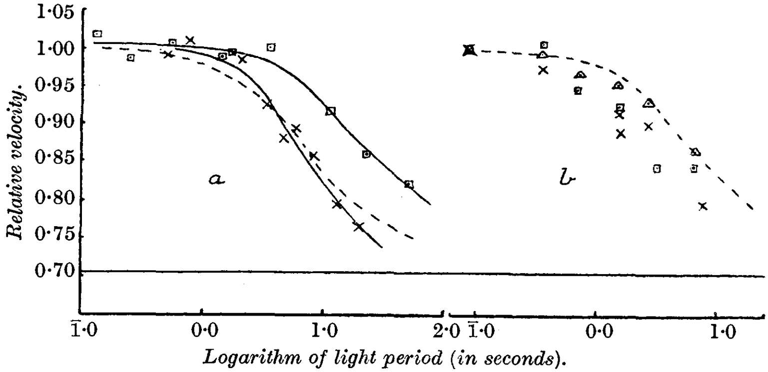
The existence of the square-root relation between velocity and intensity suggested the formation in light of a catalyst acting analogously to iodine atoms in the iodine–potassium oxalate reaction (Berthoud and Bellenot, *J. Chim. physique*, 1924, **21**, 308), and the matter was investigated further by the method of Briers, Chapman, and Walters (J., 1926, 562), a rotating sector of constant aperture but of variable rate of rotation being used. It was necessary to lower very considerably the speeds initially used before any effect was noticed, and the velocity only began to fall off when the duration of a single light (or dark) period had risen to about 1 sec. It was still decreasing when the illumination period had reached 51 secs. The results of two such experiments, carried out with rather different and unmeasured intensities, are plotted in Fig. 2*a*. The broken line represents the theoretical curve for a catalyst of life of 1 sec., calculated from the formula of Briers, Chapman, and Walters, whilst the horizontal line gives the velocity for the same continuously acting intensity (*i.e.*, half the velocity observed in absence of the sector).

FIG. 1.



(a) $I_0^{0 \cdot 5} \times 10^4$; (b) *Square root of relative sector aperture.*

FIG. 2.



Logarithm of light period (in seconds).

Experiments on direct (true) intensity variation were next carried out with chlorine-filtered light (256 $\mu\mu$). The results (Table I) show plainly that, for light of this wave-length, under the prevailing experimental conditions, velocity (v) is directly proportional to absorbed intensity (I). As, however, the results with 365 μμ light suggested proportionality between velocity and intensity at low intensities, it seemed possible that, with 256 μμ light of very high intensity, the $I^{0·5}$ relation might hold. The limit to the direct measurement by the thermopile of the absorption of the complex beam of chlorine-filtered light had already been reached. As, however, with 365 μμ light, variation of true and of average intensity had given the same type of result, it was decided to do experiments with 256 μμ light of high intensity, using a rapidly rotating sector to control the average intensity of the beam. The results are contained in Table II. The velocity measured with the smallest sector opening was very near to the *maximum* velocity observed during the experiments recorded in Table I.

TABLE I.

$I \times 10^6$ ...	8·0	13·7	15·1	16·9	23·1	29·2	34·4	39·0
$v \times 10^5$ ...	0·805	1·42	1·53	1·78	2·46	2·96	3·44	4·10
v/I	1·01	1·03	1·01	1·05	1·06	1·01	1·00	1·05

TABLE II.

Relative sector opening	1	2	4
$v \times 10^5$	3·86	7·2	11·3
Ratio	3·86	3·6	2·83

It may be mentioned that the limiting values of γ_{365} actually obtained in the experiments plotted in Curve *a* (Fig. 1) were about 4·6 and 13·5 and would, of course, have been still higher at lower intensities, whilst the constant value of γ_{256} corresponding to the data in Table I is about 5·7. This last solution was submitted to a single experiment with 365 μμ light, and proved to be just twice as reactive at the same incident intensity as the solution used in the experiments of Curve *a*, Fig. 1. At all ordinary intensities, then, γ_{365} exceeds γ_{256} for concentrated perhydrol.

Effect of Concentration.—The first series of measurements was carried out with 365 μμ light, the concentration of the perhydrol, initially 12·10*M*, being altered in steps by the addition of distilled water until it had fallen to 1·11*M*. The thermal reaction velocities were determined and subtracted from the total velocities in light in order to obtain the net light velocity, and the absorbed energy was measured. Table III contains the results, v_d being the dark and $v_{365\,\mu\mu}$ the light velocity, both as mols./hr., and γ the quantum efficiency. The net light velocity (the table contains the results of successive duplicate experiments) rises to a maximum and then

TABLE III.

Conc.	$v_d \times 10^5$.	$v_{365\,\mu\mu}$ $\times 10^5$.	γ (mean).	Conc.	$v_d \times 10^5$.	$v_{365\mu\mu}$ $\times 10^5$.	γ (mean).
12·10	0·13	8·82 8·91	9·52	4·57	0·43	11·83	20·1
9·06	0·39	11·75 11·86	14·8	2·20	0·75	9·05 9·50	22·1
6·92	0·35	12·38 12·52	16·6	1·11	0·71	5·69 5·61	23·4

falls off as the solution is diluted, γ increases steadily throughout, and the thermal reaction velocity also increases with dilution, at all events over the greater part of the concentration range covered. The square of the quantum efficiency, when plotted against concentration, follows an equation of the type $\gamma = (k_1 - k_2[H_2O_2])^{\frac{1}{2}}$.

This remarkable increase of γ with dilution was quite unexpected, and it was thought that some positive catalyst had perhaps been introduced with the water used for dilution. A similar series was therefore carried out in which the dilution was effected by decomposing part of the peroxide by insolation as already described in Part I, measurements of velocity of decomposition being made both in 365 μμ and in 256 μμ light after each concentration change. It was at this stage that we first noticed the destruction of the fluorescent properties of the perhydrol as a result of prolonged irradiation. About 24 hours' insolation was required for effecting the first change in concentration (from 10·24 to 7·92*M*) and, as will be seen from Table IV, which contains the results of this series, the disappearance of the fluorescence was accompanied by a marked rise in the velocity of the thermal reaction, and by a decided fall in the photochemical reaction rates. Omitting the figures given by the most concentrated solution as not being comparable with the remainder, it will be seen that the results, as far as 365 μμ light is concerned, are qualitatively similar to those given by the fluorescent solution used in the first series (Table III). Further, the velocity with the chlorine-filtered light increases in the same way with dilution, passes through a maximum and falls off, the quantum efficiency altering in the same manner, absorption always being

TABLE IV.

Conc.	$v_d \times 10^5$.	$v_{256\,\mu} \times 10^5$.	$v_{365} \times 10^5$.	Relative γ_{365}.
10·24	0·32	5·74	31·44	—
7·92	0·63	4·76	18·96	1·00
6·90	0·67	4·82	20·22	1·30 (mean)
		5·00	24·30	
4·65	0·51	7·04	26·38	2·11
		7·12		
1·44	0·30	6·50	21·32	4·92

complete. The thermal velocity, however, decreases with increasing dilution, whereas, in the fluorescing solution, it rises.

The results being obviously irregular, a similar set of experiments was carried out, after the fluorescence had been destroyed by a preliminary insolation. The same general type of result was obtained, but in detail the figures were as erratic as before. Finally, the original method of dilution with distilled water was reverted to, the fluorescent impurity again being destroyed at the commencement of the experiment. The readings were carried to concentrations as low as 0·06 and 0·02M, with 365 μμ and 256 μμ respectively, and the results are contained in Table V and in Fig. 3.* They confirm the former series in all essential points.

TABLE V.

Conc.	$v_d \times 10^5$.	$v_{256\,\mu\mu} \times 10^5$.	$v_{365\,\mu\mu} \times 10^5$.	Relative γ_{365}.
9·52	1·02	8·08	46·56	1·00
7·54	1·18	8·26	46·20	1·17
4·95	1·04	9·30	53·84	1·89
2·79	0·99	9·46	52·96	3·06
1·39	0·70	10·72	50·75	5·55
0·671	0·66	10·76	25·68	5·67
0·201	0·28	12·70	14·08	9·93
0·060	0·16	15·04	3·56	7·94
0·021		11·16		

Temperature Coefficient.—This was determined for the concentrated perhydrol and for the 365 μμ line only. Measurements were made at 11°, 14·5°, 21°, and 26°, and the thermal reaction velocity was roughly measured at 21° and 31°. The latter had a temperature coefficient of about 2·1 (no precise significance is attached to this figure), and at 21° accounted for 3% of the total reaction. From the smoothed curve passing through the plot of the corrected light velocities, a value of 1·39—1·40 was read off for the photochemical temperature coefficient.

B. *Experiments with Hydrogen Peroxide prepared in the Laboratory.*

The totally unexpected nature of the relations observed when using high light intensities and high concentrations of perhydrol made it very desirable to repeat the work with a material definitely free from any substance, such as the fluorescent impurity or its decomposition products, which might conceivably affect the results. Experiments were therefore carried out with hydrogen peroxide prepared ourselves by the method already described.

Preliminary Experiments.—These were done essentially in order

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* In Figs. 3, 4, and 8, the various graphs for relative quantum efficiency are in no sense comparable with others on the same diagram, each being plotted on its own arbitrary scale along the ordinate.

to confirm or otherwise the effect of concentration change noted above. Commencing with concentrated peroxide, and then working with weaker solutions prepared by dilution with water, the light velocities were determined for the 365 μμ line and for light transmitted by the chlorine–bromine filter (275 μμ). At the same time, as the thermal velocities were now sufficiently high, they also were accurately determined. The results are contained in Table VI, and in Fig. 4 are plotted, as functions of concentration, the relative quantum efficiencies for the light reactions and the unimolecular thermal reaction velocity coefficient (*i.e.*, rate of decomposition per unit mass of peroxide). The results are similar to the former ones in general outline (the continued rise of γ_{365} appears, in the light of other data, to be perhaps due to experimental error).

FIG. 3.

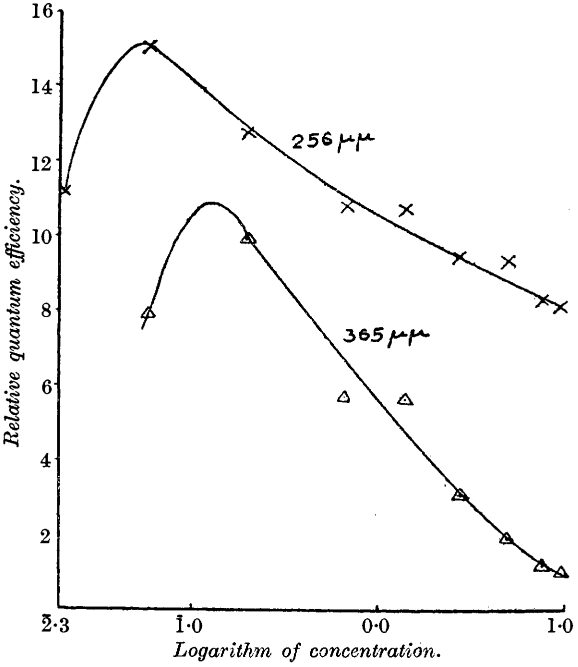


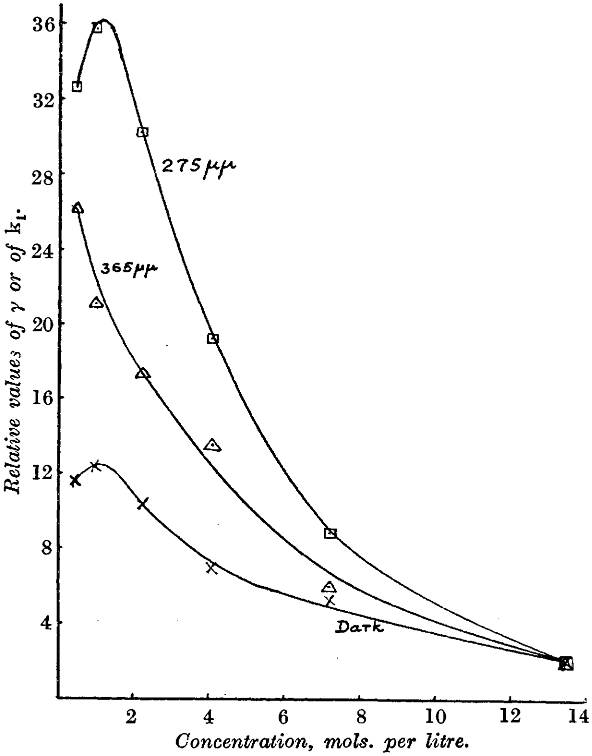
TABLE VI.

Conc.	13·44	7·19	4·04	2·21	0·98	0·475
$v_d \times 10^5$	0·98	4·65	5·70	4·89	2·56	1·13
$v_{365\,\mu\mu} \times 10^5$	17·66	69·7	98·8	74·0	41·4	25·6
$v_{275\,\mu\mu} \times 10^5$	2·38	12·31	16·36	24·60	29·16	27·42

Effect of Concentration, Wave-length, and Intensity on Quantum Efficiency.—Two systematic series of experiments were undertaken.

In the first, an 11·5M-solution was successively insolated with 365 μμ light of a whole range of measured intensities, and then by light transmitted by the chlorine–bromine filter (275 μμ region), a series of different intensities again being used. The solution was then diluted by addition of water to 5·45M, and insolated in a similar fashion, the whole process being repeated for concentrations of 2·45, 1·19, and 0·48M. The second series resembled the first, except that beams of 365 μμ and 307 μμ (average) light were employed, the concentrations being 10·17, 6·05, 3·69, 1·92, 0·95, and 0·62M. The reason for not investigating the action of the three wave-lengths on the same solution was the necessity of minimising the changes in concentration caused by the photodecomposition. Just as in the measurements already described, no great accuracy is claimed for the figures, owing to certain disturbing factors imperfectly controlled (four experiments in the second series have been neglected on this account), nor are the absolute values of any

FIG. 4.



particular interest, in view of the whole nature of the reaction. Table VII contains typical specimens of the experimental data. In all cases, the area illuminated by the incident converging beam was 5·6 cm.^{2}. Col. 1 gives the intensity in terms of incident quanta/hour/cm.^{2} × 10^{-18}, col. 2 the total quanta absorbed per hour × 10^{-18}; and col. 3 the total molecules of peroxide decomposed per hour × 10^{-19}.

FIG. 5.

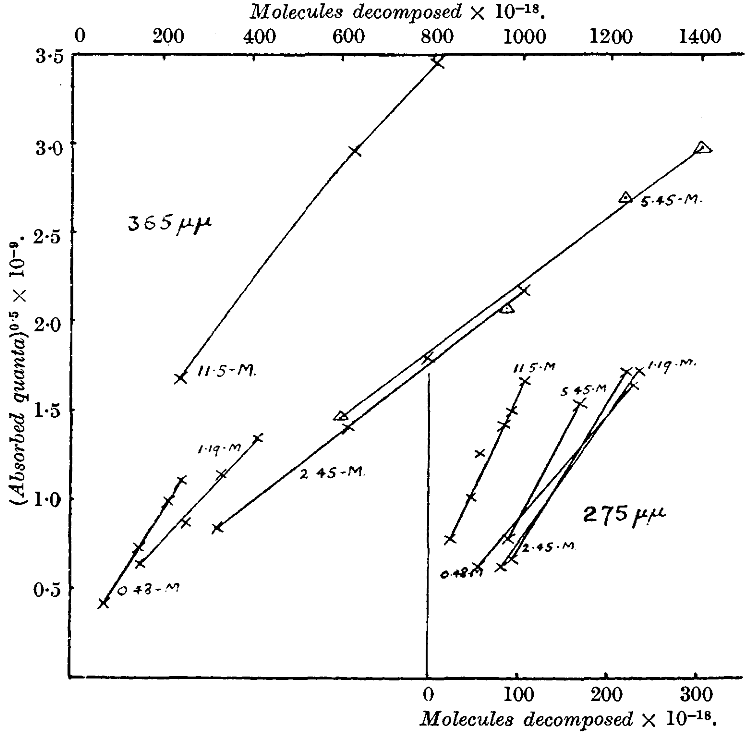


TABLE VII.

(a) Series I.

275 μμ; 1·19M-H_2O_2.

(1).	(2).	(3).
0·0684	0·383	7·40
0·165	0·927	12·5
0·259	1·47	17·7
0·412	2·31	19·6
0·531	2·97	23·6

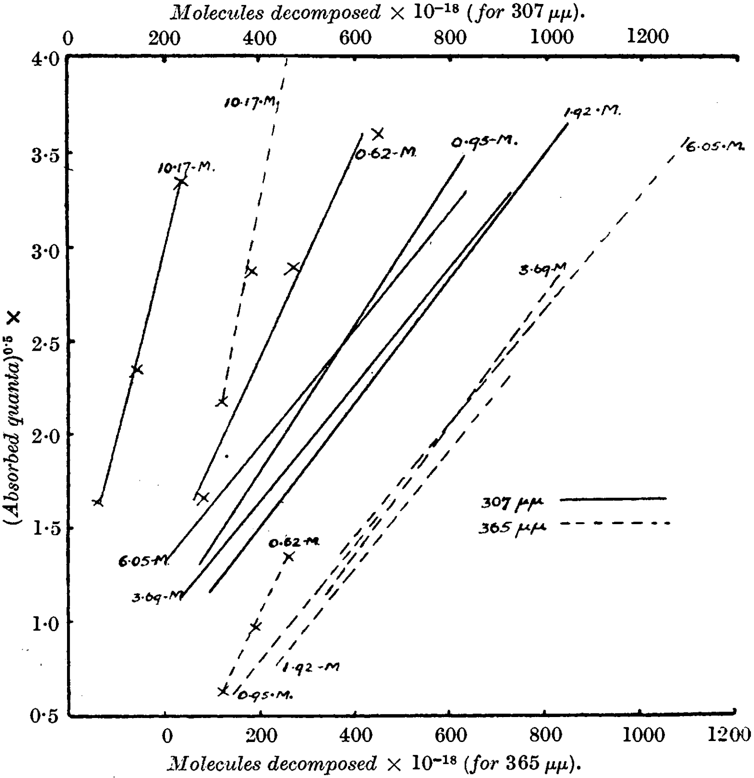
(b) Series II.

365 μμ; 3·69M-H_2O_2.

(1).	(2).	(3).
0·902	1·23	33·9
1·56	2·13	42·5
4·23	5·75	75·8
5·63	7·56	82·4
5·88	7·99	78·9

The results as a whole are shown in Figs. 5 and 6, where the square root of the number of quanta absorbed per hour is plotted against the number of molecules decomposed per hour. In order not to confuse the diagrams, the actual experimental points in many cases are not put in, but merely the best line drawn through them. Further, in both diagrams, and in order to economise space, the curves for 365 μμ light and for the most concentrated peroxide solution are not completely shown. It will be obvious that the quantum efficiency for any particular concentration and rate of energy absorption can be read off by dividing the abscissa by the square of the ordinate.

Fig. 6.



It will be noticed that, with one exception, *viz.*, 11·5*M*-peroxide and 365 μμ, the curves are linear. Although it will appear later that, in one or two cases, this linearity is only apparent and due to experimental error and the scale of plotting, we are nevertheless justified in concluding that, in general, over our working range of concentration and intensity, any increase in velocity is proportional to the corresponding increase in the square root of the intensity, whatever the wave-length of the light. It will further be noticed that the majority of the curves, if produced, do not pass through the origin, but cut the ordinate. This fact is reminiscent of Curve *a* (Fig. 1); its significance will be discussed later.

With regard to the relative values of the quantum efficiencies obtained at any given rate of absorption of quanta, it will be seen (*a*) that, in general, γ_{365} is greater than γ_{307} and γ_{275}; (*b*) that the γ_{365} values are considerably higher in Series I (Fig. 5) than in Series II (Fig. 6); (*c*) that, as the concentration falls, γ increases in every case, and usually passes through a maximum at some intermediate concentration and falls off in dilute solution. Conclusions (*a*) and (*c*) are in accordance with the results obtained with perhydrol insolated by 256 μμ and 365 μμ light. The absolute values of γ naturally vary between wide limits, roughly 20—500, depending on wave-length, intensity, concentration, and the particular solution used.

Effect of Intermittent Illumination.—It was clearly desirable to see whether the "pure" hydrogen peroxide solutions behaved in the same manner as did perhydrol during intermittent insolation with light and dark periods of varied length. Measurements were done with 307 μμ light, a new cell with well-annealed surfaces being used, together with a temperature of 2° so as to minimise thermal decomposition. Three concentrations were employed, *viz.*, 11·0, 6·4, and 3·3*M*. The method of experimentation was as already described, the duration of a single reaction always extending over at least 100 intermissions. The data are contained in Fig. 2*b*, where the broken line again represents the theoretical curve for a mean life of 1 sec., whilst the horizontal line denotes the decomposition for the same continuous intensity. The results are clearly subject to considerable error, but suffice to show that the mean life of the presumed catalyst rises with dilution and is about 0·4 sec. for 11*M*-solutions. No exact comparison between Figs. 2*a* and 2*b* can be made, for the light intensities used were not measured, whilst the solutions were of different origin. It would seem likely, however, that the mean life of the catalyst increases with the wave-length of the active light.

Temperature Coefficients.—These were determined for three concentrations and for three wave-lengths, two measurements being made at each temperature, *viz.*, 2° and 22°. The temperature coefficient of the thermal reaction was necessarily measured at the same time. The results are contained in Table VIII, from which it would appear that any effect of concentration is within the limits of experimental error.

TABLE VIII.

Conc.	Temperature coefficients. Thermal.	365 $\mu\mu$.	307 $\mu\mu$.	275 $\mu\mu$.
10·5M	2·96	1·43	1·35	1·26
7·3M	2·66	1·39	1·38	1·28
1·3M	2·87	1·45	1·40	1·29
Mean values	2·83	1·42	1·38	1·28

Previous results for the photochemical reaction are as follows, T.C. denoting the temperature coefficient :

Worker.	T.C.	Conditions of experiment.
Tian	1·15	Thin layers of dilute perhydrol. Centre of gravity of absorbed light probably 260 $\mu\mu$.
Kornfeld	1·32	Dilute solutions of perhydrol. Uviol glass apparatus. Light chiefly absorbed 313 $\mu\mu$.
Matthews and Curtis	1·5	Uviol lamp radiation passed through several thicknesses of Uviol glass. Dilute perhydrol. Active light probably chiefly 365 $\mu\mu$. Thermal reaction not corrected for.
Anderson and Taylor	1·43	Pure dilute solutions. Full light of quartz mercury lamp in quartz vessels.

Our value for concentrated perhydrol and 365 $\mu\mu$ was 1·39—1·40.

C. *Experiments with Dilute Solutions.*

One of the most striking of the results recorded in sections A and B is the passage of γ through a maximum as the peroxide concentration is increased. It was clearly desirable to investigate rather more fully the behaviour of solutions of low concentration, particularly in view of the statement frequently made that the reaction is of the first order.

Some of our earliest experiments, carried out on dilute solutions of Merck's peroxide containing a nitrogenous inhibitor, were of this nature, the 5-mm. wax-lined cell (described at the end of Part I) being used, and the initial rates of reaction of a series of solutions of different concentrations being measured both in the full light of the lamp, and also in light which had been passed through a 2-cm. chlorine filter. They gave the same type of velocity–concentration curve. The results obtained with the chlorine-filtered light are shown in Figs. 7*a* and 7*b*. The former contains, plotted against concentration, the relative measured velocities and the relative quantum efficiencies, these being calculated from a knowledge of the energy distribution in the filtered beam and the extinctions of the different solutions. Fig. 7*b* shows the velocity plotted against (*a*) the light absorption, (*b*) the square root of the light absorption. Although the points are irregular, the best straight line drawn through the latter set passes through the origin on being produced.

A similar experiment (5-cm. chlorine-filter; 256 $\mu\mu$) was carried out on a dilute solution of the pure peroxide, which was initially 1·8*M* and decomposed during the insolation down to a final concentration of 0·1*M*. Here the behaviour was quite different, γ

FIG. 7.

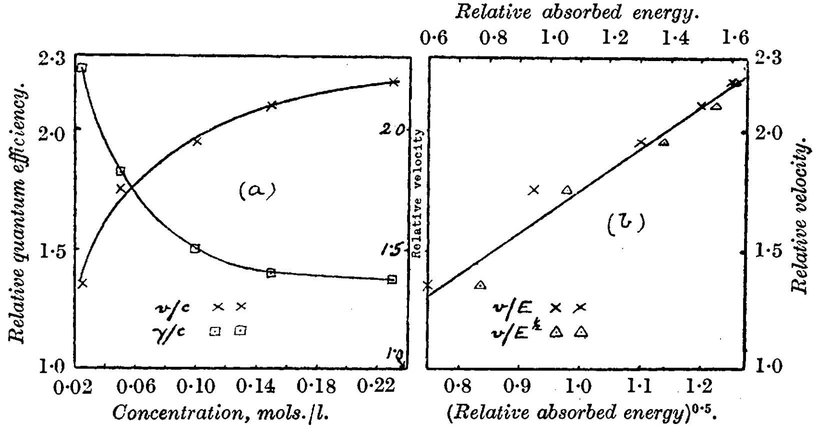
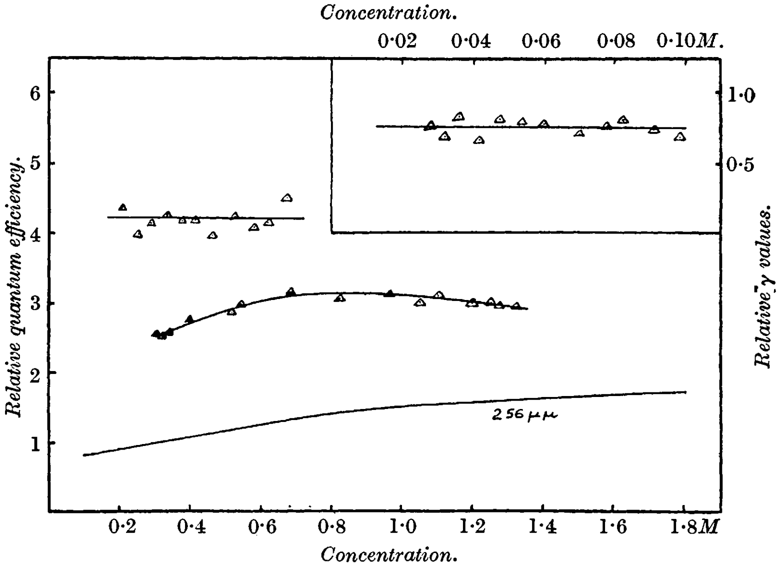


FIG. 8.



dropping throughout as the concentration fell (Fig. 8). Above 0·3*M*, absorption of the active light was practically complete. The curve has been drawn from the smoothed experimental data.

Finally, a number of experiments were carried out with dilute solutions of the pure material and 365 μμ light, using the methods described at the end of Part I and following the reaction by measuring the evolved oxygen. The relative quantum efficiencies for three such experiments, calculated by dividing the velocities by the average concentration between each pair of points, are shown in Fig. 8. No very definite conclusion can be drawn from them and the experiments clearly need extension.

D. *Summary of Experimental Results.*

Figs. 5 and 6 exhibit the results of two comprehensive series of experiments in which the effects of variations in λ, I_0, and $[H_2O_2]$ on the photolysis were investigated, specimen detailed figures being tabulated in Table VII. In the majority of cases, the observed velocity can be plotted, within the limits of experimental error, linearly against the square root of the rate of absorption of energy, the curves appearing, when produced, either to pass through the origin or to cut the energy axis. Experimental error and the scale of plotting both forbid their closer analysis, which is best achieved by calculating from the original data relative values of the characteristic k_A constants (J., 1929, 1557) by means of the formula

$$-\Delta u = k_A \,.\, I_0^{\frac{1}{2}} \,.\, \frac{2}{c^{\frac{1}{2}}\alpha^{\frac{1}{2}}} \,.\, (1 - 10^{-\frac{1}{2}\alpha cl})$$

where, in the present case, $-\Delta u$ is the number of molecules of peroxide decomposed per hour, I_0 the total number of quanta incident per hour per cm.^{2} on the illuminated area of the cell, c the concentration in mols./litre, α the average extinction coefficient for the incident light, and l the depth of the cell (5 cm.). With the exception of four readings in Series II, which were clearly in serious error, all the data have been calculated in this way, the extinction coefficients used being 0·0066 for 365 μμ, 0·59 for 307 μμ, and 6 for 275 μμ. For the 275 μμ experiments, and for all but the two weakest solutions with the 307 μμ light, the term $1 - 10^{-\frac{1}{2}\alpha cl}$ is practically unity, the expression simplifying to

$$-\Delta u = 2k_A I_0^{\frac{1}{2}}/c^{\frac{1}{2}}\alpha^{\frac{1}{2}}.$$

Table IX contains in detail the values of $k_A \times 10^{-11}$ calculated from the readings of Series I with 275 μμ light, arranged in each case in order of ascending values of I_0 (not given; they varied between limits of 0·068—0·531 × 10^{18} quanta/hour/cm.^{2}).

The constancy of the k_A values for the three intermediate concentrations indicates that, over the whole intensity range covered, except for the lowest intensity with the 1·19*M*-solution, the velocity is proportional to $I_0^{0{\cdot}5}$. This relation clearly does not hold either

TABLE IX.

Values of $k_A \times 10^{-11}$.

	11·5*M*.	5·45*M*.	2·45*M*.	1·19*M*.	0·48*M*.
	3·20	7·51	5·79	(3·77)	1·92
	4·77	7·55	6·04	4·11	2·34
	5·00	7·93	5·30	4·65	2·57
	5·86	7·36	6·89	4·08	3·16
	6·22		5·07	4·33	
	6·43		5·44		
Means	—	7·59	5·92	4·29	—

for the weakest or for the strongest solution, and reference to Fig. 9 shows that the I_0 rule is obeyed by the 11·5*M*-solution and possibly by the 0·48*M*-solution (points very scattered).

FIG. 9.

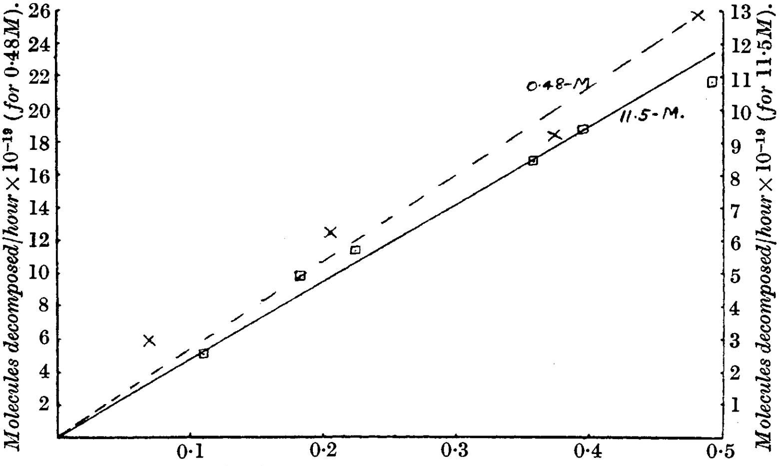


Table X contains a summary of all the results in the form of the mean values of k_A holding for any particular wave-length and concentration. In two further cases with concentrated solutions, apart from that just mentioned, the values were found to drift, as the intensity was raised, in a direction which showed that the $I_0^{0 \cdot 5}$ rule was breaking down at low intensities, and being replaced by the I_0

TABLE X.

Series I.			Series II.		
$[H_2O_2]$.	275 μμ.	365 μμ.	$[H_2O_2]$.	307 μμ.	365 μμ.
11·5*M*	3·20 → 6·43	1·01 → 1·91	10·17*M*	1·13 → 2·08	0·42
5·45	7·59	(2·86)3·28	6·05	5·85	2·09
2·45	5·92	(2·72)3·13	3·69	4·97	2·13
1·19	(3·77)4·29	(1·72)2·12	1·92	3·61	2·21
0·48	1·92 → 3·16	(1·32)1·61	0·95	2·09	1·93
			0·62	1·38	1·43

rule. In addition, in Series I with 365 $\mu\mu$ light, the k_A values obtained with the lowest intensity used (figures in brackets) were always lower than those subsequently found, indicating again that the $I_0^{0·5}$ rule was not being fully obeyed under such conditions.

Taking into account the various differences manifested in the above tables, we can summarise the main results of our experimental work as follows :

(1) Over wide ranges of I, λ, and [H_2O_2], the rate of photolysis is proportional to $I_0^{0·5}$. This behaviour is favoured by high intensities (Fig. 1, Tables II, IX, X); with low intensities, a tendency towards a reaction of the I_0 type becomes apparent. At very high and at low concentrations (Fig. 9; Tables IX, X; also previous results of Tian and of Henri and Wurmser, *locc. cit.*), the velocity tends to be proportional to the intensity.

(2) The velocity at constant incident intensity passes through a maximum as [H_2O_2] is increased and then falls off (Tables III, IV, V, VI).

(3) In some cases, γ also passes through a similar maximum with increase in [H_2O_2] (Tables IV, V; Figs. 3, 4, 5, 6, 8). This is not always the case in the concentration range studied (Tables III, IV; Figs. 4, 5, 8).

(4) Under our experimental conditions γ tends to be high; there is a catalytic chain with a life of about 1 sec., becoming less with increase in concentration and probably also with increase in frequency (Fig. 2).

(5) Both γ (tables and diagrams) and temperature coefficient (Table VIII) under the prevailing conditions fall off as the frequency of the light is increased, the temperature coefficient doing so to an extent independent of concentration.

(6) A dilute solution of hydrogen peroxide containing inhibitor decomposes with a velocity which rises with increase in concentration at a rate proportional to the square root of the rate of the absorption of energy (Fig. 7).

(7) The velocity of thermal decomposition of peroxide solutions passes through a maximum and subsequently falls off as [H_2O_2] increases. In one case (Fig. 4), the corresponding unimolecular velocity coefficient–concentration curve also has a maximum; other data (Tables IV, V) give no such maximum. The temperature coefficient of the rate of thermal decomposition is normal, and is independent of [H_2O_2] over the concentration limits tested (Table VIII).

E. *Discussion.*

To explain these very complex relations (many of them unexpected, *e.g.*, the effect of intensity in the intermediate concentration range, the relations between γ and λ and between [H_2O_2] and velocity) on a simple basis is clearly impossible, and we shall at present confine ourselves to a brief discussion of some of the more salient points.

(i) Any satisfactory theory of the photolysis of hydrogen peroxide solutions must first of all take into account the great similarity between the photochemical and thermal reactions. This is apparent throughout, and particularly so in Table VI, where, except for the lowest concentration employed, the thermal velocity and the velocity in 365 $\mu\mu$ light are practically proportional to one another within the experimental error.

(ii) The next point to emphasise is the effect of dust particles as demonstrated by the work of F. O. Rice and his collaborators. The photochemical, and hence presumably the thermal, reaction is a chain reaction, and the question arises as to whether it is the initiation or the continuation (or both?) of the chain which is a surface reaction. Recent workers (Williams, *Trans. Faraday Soc.*, 1928, **24**, 245; Pana, *ibid.*, p. 486) on the thermal reaction conclude that it is *initiated* on the surface of the vessel or on dust particles.

(iii) We find the temperature coefficients of the photolysis to decrease with increasing frequency, but to be independent of concentration. This strongly suggests that they are concerned with the primary process only. Calculating the molar energy of activation (E) by the method of Arrhenius, we find $E_{365\,\mu\mu} = 5850$, $E_{307\,\mu\mu} = 5380$, $E_{275\,\mu\mu} = 4120$ cals. With Tolman (*J. Amer. Chem. Soc.*, 1923, **45**, 2285), we can equate E to $N(\bar{\bar{\varepsilon}} - \bar{\varepsilon})$, where $\bar{\varepsilon}$ represents the average energy of all molecules of peroxide and $\bar{\bar{\varepsilon}}$ the average energy (before absorption) of those molecules which are sufficiently activated by quantum absorption to be capable of initiating a reaction chain. The fraction of molecules (f) in this potentially reactive state ($\bar{\bar{\varepsilon}}$) in respect of light of a particular wavelength will be given by $e^{-E/RT}$, from which we obtain $f_{365\,\mu\mu} = 4 \times 10^{-5}$, $f_{307\,\mu\mu} = 9 \times 10^{-5}$, $f_{275\,\mu\mu} = 80 \times 10^{-5}$.

If this view is correct, it appears that only a very small proportion of the absorbing molecules react subsequently to absorption, and that therefore the reaction chains must be exceedingly long—of the order of 10^4 to 10^7 links, leaving out of account any deactivation (by whatever means) experienced prior to the inception of the chain.

(iv) The $I_0^{0.5}$ relation suggests that the catalyst (of mean life about 1 sec.) which is responsible for the reaction chain may consist either of hydroxyl groups or of oxygen atoms, produced in the liquid phase in accordance with one of the equations

$$H_2O_2 + h\nu \longrightarrow 2OH,$$
$$H_2O_2 + h\nu \longrightarrow H_2O + O,$$

and, when their rate of production per unit volume is sufficiently high, disappearing in accordance with either

$$2OH \longrightarrow H_2O_2 \text{ (or } H_2O + \tfrac{1}{2}O_2\text{)},$$

or

$$2O \longrightarrow O_2.$$

Thermochemically, these two primary light actions are both possible, the former absorbing 56·5 Cals. (calculated from the work of Bonhoeffer and Reichardt, *Z. physikal. Chem.*, 1928, *A*, **139**, 75) and the latter 56·8 Cals. Referred to a single molecule, these figures correspond to a light quantum at about 500 $\mu\mu$, *i.e.*, in the blue-green region of the spectrum, whereas the longest wave-length used by us was 365 $\mu\mu$.

(v) To account for the validity of the I_0 relation at low intensities and concentrations, and also at high concentrations, additional hypotheses are necessary. For example, we have tested the assumption that, the hydroxyl group being the catalyst, it can be removed unimolecularly in certain circumstances by adsorption on dust particles, and, under other conditions, by combination with peroxide molecules to form unstable H_3O_3 molecules which then rapidly react with one another. If the " chain " be supposed to be initiated by impact of such hydroxyl groups on the layer of peroxide molecules adsorbed on dust particles, and if a further type of " deactivating " collision involving peroxide molecules be introduced, then the majority of the experimental facts found by us can be brought into line. Some, however, remain unexplained. For example, the predicted behaviour of solutions of concentration 2*M* and less is not completely in accord with the (rather uncertain) experimental data, and further work is being done in this direction. Until the results of these experiments are available, it is of little use to discuss further either the explanation of our own results or their relation to the work of others.

(vi) Two particular points may be mentioned in conclusion. (1) Our results with the dilute solution containing inhibitor (Fig. 7) can readily be explained on the mechanism referred to above. (2) This point relates to the values for the empirical experimental constant k_A, contained in Table X. They vary with concentration, which merely shows at present that the photolysis is a complex one, but are also seen to rise with increasing frequency (see J., 1929, 1537) and not to decrease, as is the case with the values of γ. On the theory outlined above, they should be proportional to the square root of the coefficient (k_1) which measures the efficiency of the primary dissociation process following on quantum absorption.

These k_1 values are proportional to the f values calculated above, and we consequently have

$$(k_1)_{365\,\mu\mu} : (k_1)_{307\,\mu\mu} : (k_1)_{275\,\mu\mu} = 4 : 9 : 80$$

and hence

$$(k_\text{A})_{365\,\mu\mu} : (k_\text{A})_{307\,\mu\mu} : (k_\text{A})_{275\,\mu\mu} = 2 : 3 : 9.$$

There is no quantitative coincidence between these ratios and the varying figures contained in Table X, but the fact that the admittedly incomplete theory gives even the found measure of agreement is of interest.

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