LXXXI.—*The Photolysis of Aqueous Hydrogen Peroxide Solutions. Part I. Experimental Methods.*

By Arthur John Allmand and Derrick William Graham Style.

The decomposition of hydrogen peroxide solutions by light has been the subject of a number of previous investigations (Tian, *Compt. rend.*, 1910, **151**, 1040; 1913, **156**, 1601, 1758, 1879; *Ann.*

Fac. Sci. Marseille, 1915, **22**, 197; *Ann. Physique*, 1916, **5**, 248; Henri and Wurmser, *Compt. rend.*, 1913, **156**, 1012; **157**, 126, 284; *J. Physique*, 1913, **3**, 305; Matthews and Curtis, *J. Physical Chem.*, 1914, **18**, 166, 521; Kornfeld, *Z. wiss. Phot.*, 1921, **21**, 66; Anderson and Taylor, *J. Amer. Chem. Soc.*, 1923, **45**, 650, 1210; Rice and Kilpatrick, *J. Physical Chem.*, 1927, **31**, 1507), but in spite of this work, and although the reaction is, chemically, very simple, very little can be said about its mechanism, many points remain obscure, and there are some very curious contradictions. One of the more obvious may be mentioned: Henri and Wurmser published, in the same year, two papers (*loc. cit.*) dealing with the quantum efficiency of the reaction in the region 200—300 $\mu\mu$; in the one, using full light from a cadmium spark, they found γ to have an average value of 130; in the other, using the dispersed light from a zinc spark, they found γ over practically the same spectral region to vary between 4·4 and 5·8.

Our work has been essentially directed to an investigation of the relations between degree of decomposition and absorbed light over a wide range of concentration, far greater than any hitherto worked with. In the majority of the experiments, the active light has been monochromatic or confined to a fairly narrow spectral region. Except quite incidentally, we have not touched the subject of the effect of additions to the photolyte, whether inhibitors or accelerators.

EXPERIMENTAL.

Hydrogen Peroxide.—Three different varieties were employed. Some early experiments with dilute solutions were carried out on a specimen of perhydrol (Merck) intended for tropical export, and containing a nitrogenous thermal inhibitor. For much of the work, Merck's ordinary perhydrol (inhibitor-free) was used. When first insolated by 365 $\mu\mu$ light, this showed a strong bluish-green fluorescence, which decreased normally on dilution. Continued insolation completely destroyed this fluorescence, and its disappearance was accompanied by a marked decrease in the photosensitivity of the perhydrol, but by an equally marked increase in its rate of thermal decomposition. It is probable that the impurity causing the fluorescence was derived from the wax with which the perhydrol bottles are internally coated: this is yellow and has a distinct oily smell. It may be added that we found it very difficult to inhibit the photodecomposition of the concentrated perhydrol. Small additions of sulphuric acid to the cell contents were without effect, whilst 1 g. of concentrated acid only reduced the velocity by 30—40%.

The remainder of our experiments were carried out on hydrogen peroxide prepared in the laboratory by the method of Kilpatrick, Reiff, and Rice (*J. Amer. Chem. Soc.*, 1926, **48**, 3019), modified in certain respects. In the actual distillation of the first product, 200 c.c. were placed in the glass distilling flask, and the remainder added in 50-c.c. portions as the distillation proceeded. The flask had a volume of 500 c.c. and its neck was provided with two ground joints, one of which carried a thermometer suspended by platinum wire from the stopper, the other a tap-funnel for the addition of more solution. The outlet tube was bent upwards and terminated in a ground joint making connexion with the silica condenser, to which was attached, by another joint, the silica receiver. No lubricant other than condensate was employed on any of the joints, and practically no leakage resulted under the water-pump vacuum conditions (2 cm. of mercury) employed. The first 80% of the distillate consisted of a weak solution of hydrogen peroxide (0·1—0·3*M*) and was discarded. The final concentrated fraction was freed from traces of chloride by redistillation over small quantities of silver sulphate. The solutions thus prepared were 9—14*M*.

Extinction Coefficients.—These were determined for the chief lines of the quartz–mercury arc by the spectrometer–thermopile–galvanometer method, the transmissions of a small quartz cell filled with distilled water and with the peroxide solution being compared. For 365 μμ the cell was 4·62 cm. deep (internal) and several concentrations were measured. For 313 and 303 μμ, a 2·04-cm. cell was used, and one concentration only was investigated. For the shorter wave-lengths, the cell was 1·026 cm. deep and various concentrations were used. Table I contains the molecular extinction coefficients for redistilled Merck's perhydrol, calculated by the equation $\log_{10} I_0/I = \alpha c d$, where d is expressed in cm. and c in mols./litre. The measurements with the 365 μμ line were made by Mr. J. W. T. Spinks.

TABLE I.

λ, μμ.	c.	α.	λ, μμ.	c.	α.	λ, μμ.	c.	α.
365	11·63	0·00647	365	3·08	0·00655	280	0·0758	4·06
365	9·45	0·00669	313	0·459	0·39	265	0·0758	10·03
365	7·57	0·00663	303	0·459	0·86	265	0·0287	10·48
365	5·96	0·00668	297	0·238	1·31	265	0·01125	10·33
365	4·78	0·00683	289	0·238	2·16	254	0·0287	21·9
365	3·70	0·00673	280	0·238	3·73	254	0·01125	19·6

In one paper, Henri and Wurmser quote $\alpha_{280} = 3{\cdot}0$ and $\alpha_{256} = 20$. From the data in another of their papers can be calculated $\alpha_{293} = 1{\cdot}5$, $\alpha_{275} = 4{\cdot}9$, and $\alpha_{257} = 16$. Kornfeld (*loc. cit.*) found 0·422 for 311 μμ. The agreement with these values is seen to be fairly good. On the other hand our figures are very different from those recently published by Urey, Dawsey, and Rice (*J. Amer.*

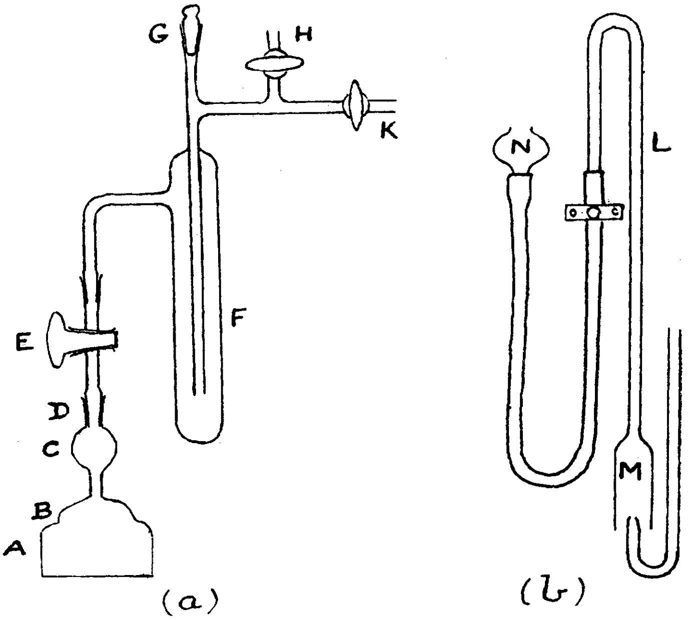
Chem. Soc., 1929, **51**, 1371), the two sets of α values only approaching one another at the shortest wave-lengths measured by us; the discrepancies seem too great to be accounted for by the fact that our solutions were more concentrated.

Reaction Cell.—The type of apparatus employed was determined by the use, in the majority of our experiments, of such concentrated peroxide solutions as to make it impossible to follow the reaction with any accuracy by titration. The method used was to pump off, collect, and measure the oxygen formed, a procedure already adopted with success in this laboratory in the case of the photolyses of formic and of oxalic acid (J., 1926, 2834, 2854). The method offered the additional advantage of reducing to a minimum the possibility of contamination during the reaction by added inhibitors or accelerators. A Toepler pump of about 300 c.c. capacity was used for the evacuation of the reaction cell, the latter being provided with a tap and ground joints so that it could be opened for filling and cleaning and for attaching to the pump for evacuation before and after insolation. Early experiments showed the importance of keeping the photolyte away from contact with glass. Attempts to use a composite cell, built up of quartz plates and a glass block, the inner surface of the latter being coated with paraffin wax, failed, as the wax peeled off when the cell was evacuated. An attempt to construct a cell consisting of quartz plates fused on to a reinforced block of paraffin wax also failed, as the cell slowly caved in and developed leaks on evacuation. Finally, a fused silica cell was designed, with which, or its successor, the great majority of our results were obtained. This, with the adjacent parts of the Toepler pump, is shown in Fig. 1*a*.

ABCD is of clear fused quartz, the part A, through which the light beam passed, being 5 cm. long with circular plane parallel end-plates of 3 cm. diameter. B is a hemi-cylindrical dome, giving an adequate surface of liquid for evolution of oxygen, and ensuring that the level of the photolyte shall always be well above that of the beam of light. C is a bulb, serving to retain any peroxide carried up by " bumping " or by too violent an evolution of gas. Into the ground socket D fits the glass tap E, provided with another ground socket at its upper end, allowing of connexion with the evacuation apparatus. F is a trap in which, during evacuation, vaporised hydrogen peroxide and water vapour are condensed by immersion in an ether–solid carbon dioxide mixture. It is provided with a stopper G for removing this condensate when necessary. H is a tap for admittance of air, and connexion with the pump (300 c.c. barrel) is made through the tap K. Ramsay tap-grease was used for all taps and joints.

Measurement of Evolved Gas.—Fig. 1*b* shows the simple means employed for the measurement of the evolved gas. The inverted U-tube L was of about 3 mm. internal diameter (and thus of internal volume 0·070 c.c./cm.) and its longer limb was 40 cm. long. The extension M permitted of the introduction of the delivery tube of the Toepler pump. The shorter limb was connected by pressure tubing, controlled by a screw clip, with the mercury reservoir N. Prior to the collection of a sample of gas, the whole tube was filled with mercury and the screw clip closed. The gas was then pumped off and delivered into M, the diameter of L being sufficiently small to prevent the gas rising further. On the completion of the evacuation, the latter was drawn into L by manipulation of N and of the screw clip, its temperature and pressure measured, and the length of the column read off by means of a scale placed immediately behind L.

FIG. 1.



(a) (b)

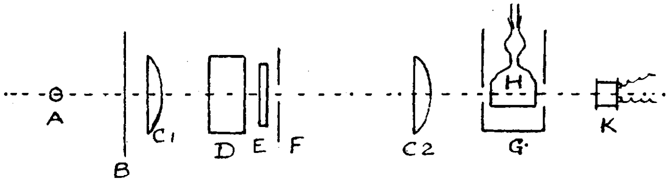
Manipulation.—In view of the importance of the nature of the surface in all work with hydrogen peroxide, the treatment to which the reaction cell was subjected was as far as possible standardised. Before being filled, it was first cleaned with nitric acid containing a small quantity of alcohol, grease on the ground joint being thereby removed, and, after a thorough washing with distilled water, it was rinsed out several times with a portion of the reaction solution, and filled nearly up to the dome. The ground joint D (Fig. 1*a*) was then lightly greased and put in position, being held down by rubber bands passing over the tap E and round the bottom of the reaction cell. E was very carefully greased and put together. It was of the utmost importance that this tap should function well, as it sometimes had to be turned several hundred times in the course of a series of experiments done on a single filling. The whole was then attached to the pump and evacuated as far as possible, E being opened at intervals. Continual attention (tapping and shaking of the cell) was necessary to avoid explosive bumping and gas evolution. The degree of evacuation feasible was limited by the thermal decomposition of the peroxide. With Merck's perhydrol, this was slow and caused no trouble. With the solution prepared by us, where the dark reaction for the cell contents might amount to perhaps 0·02 c.c. of oxygen per min., the method of evacuation had to be carefully standardised and its results watched in order to detect the stationary state at which the rate of removal of oxygen was just equalled by its rate of production.

The moment of completion of the evacuation was noted and taken as the zero time of the dark reaction for which correction had subsequently to be made. With taps E and K closed, air was admitted by opening H, the cell detached, placed in the thermostat (see later), allowed to reach temperature equilibrium, and the insolation commenced. After the required interval (varying from a few minutes to a few hours) the cell was again attached to the pump, the tap H closed, and, after the evacuation of the air between E and K (sometimes carried out through H by a Hyvac pump in order to accelerate matters and reduce the " dark " correction), the gas in the cell was pumped off, collected, and measured as quickly as possible.

With perhydrol, the " dark " correction was usually only a few units %, and the duration of an insolation of the order of an hour. As already indicated, work with the solution prepared by us in the laboratory was far less easy. The quantum efficiencies were raised 10—20-fold, and the thermal reaction to an even greater extent. As the amount of decomposition permissible in a simple insolation was limited (*a*) by the desirability of avoiding any appreciable change in the concentration, and (*b*) by the possibility of too high a pressure loosening the joint D, it became necessary to reduce the time of insolation considerably, runs of 4 mins. not being uncommon. But clearly the time necessary for the evacuation and collection of the gas could not be reduced to anything like the same extent; even if the Hyvac pump was used whenever possible, 15—20 minutes was about the shortest time required. Consequently, the thermal correction was considerable with this preparation—indeed, it was impossible to obtain results of value in the use of mercury light filtered by a chlorine filter (*q.v.*), where the intensities were comparatively low, for the thermal reaction considerably exceeded 50% of the total decomposition.

Arrangement of Apparatus for Insolation Experiments.—The general arrangement is shown in Fig. 2; A represents the source of light, B is a shutter, and C_1 and C_2 are crystal quartz lenses. D is a 5-cm. quartz water-cell, E the light filter, F a diaphragm with variable aperture (0·5—2·5 cm. diameter), and G a small thermostat containing the reaction cell H. Finally, K is the thermopile for the measurement of the incident and absorbed energy. All apparatus when necessary was firmly secured to an optical bench and, with the exception of the lamp and shutter, was covered by an internally blackened box, C_1 being fitted into a hole cut in the side.

FIG. 2.



Light Source.—In every case this consisted of a K.B.B. quartz mercury lamp of the atmospheric pressure type; these had an advantage over the vacuum type for the present work because of their relatively high intensity, this being due to the short length of arc and to the fact that they can be overloaded and yet burn very steadily, provided that additional cooling be employed. We used 100—110-volt lamps, both of the horizontal and of the vertical pattern. Their normal rating is 2 amps. We burnt them at 3·5 amps. and 80 volts, a Tirrill regulator ensuring a steady supply voltage, and the lamps being cooled by an electric fan. The energy distribution of their radiation, a knowledge of which was necessary in consequence of the light filters not being monochromatic, was determined on several occasions during the work by a modification of standard methods already described (*J. Physical Chem.*, 1925, **29**, 713). An example of the data obtained is given in Table II, *I* being the intensity relative to the 365 $\mu\mu$ line as unity.

Light Filters.—Four types of filter were used.

(*a*) Corning Glass Plate G.586 A.W. of 3·6 mm. thickness. Transmission — 0·77 of 365 $\mu\mu$ and 0·22 of 405 $\mu\mu$; 7% of the total radiation transmitted, when used in conjunction with the 5-cm.

TABLE II.

Horizontal arc, after 50 hours' running.

λ, μμ.	*I.*	λ, μμ.	*I.*	λ, μμ.	*I.*	λ, μμ.	*I.*
579	0·85	365	1·00	289	0·029	265	0·094
546	0·68	313	0·44	280	0·054	260—254	0·170
436	0·56	303	0·20	275	0·015	248	0·032
405	0·30	297	0·091	270	0·019	240—239	0·012

water filter, was red and infra-red. This correction was determined by means of a thermopile and a Zeiss red-glass filter which cuts off sharply below 600 μμ whilst transmitting about 85% of radiation between this limit and nearly 2 μ. The violet 405 μμ light is not appreciably absorbed by hydrogen peroxide.

(*b*) 1 Cm. of 0·1% aqueous potassium chromate solution between quartz plates. The transmission was

579	546	436	405	313	303	297 μμ
0·80	0·88	0·71	0·63	0·44	0·39	0·30

10·3% of the total transmitted radiation was red and infra-red. The visible light is not absorbed by hydrogen peroxide.

(*c*) 5 Cm. of chlorine gas at 1 atm. pressure in a plane-parallel vessel of fused silica. The transmission was

579	546	436	405	280	265	256	248 μμ
0·875	0·85	0·40	0·145	0·04	0·42	0·63	0·60

Used in combination with the mercury lamp, the average wavelength of the ultra-violet transmitted light was 256 μμ. For a few experiments, a similar 2-cm. filter was employed.

(*d*) A mixture of chlorine gas and of saturated bromine vapour in a fused quartz cell. The latter was about 4·5 cm. deep and of poor quality, the end plates not being accurately parallel. The maximum ultra-violet transmission of this filter is near 275 μμ and one-sixth of the light transmitted lay below 300 μμ, as determined by exposing a thermopile alternately behind glass and quartz plates.

The spectral transmissions of these filters were determined in the usual manner by means of a spectrometer–thermopile–galvanometer combination.

Thermostat.—This was of simple construction. In the square ends of an open copper box, 10 × 10 × 5·2 cm., directly opposed central holes of 2·9 cm. diameter were cut. Around them, inside the box, was soldered a copper U, reaching to the top of the box and dividing it into two compartments. The circular apertures in the inner jacket were covered with quartz plates. This inner compartment held the reaction cell during insolation and was filled with distilled water. The outer jacket contained ice or water, depending on the temperature of the experiment which was 21°

unless otherwise stated. The temperature of the thermostat could readily be controlled by addition by hand of small quantities of hot water or of ice. A small heating coil was sometimes used.

Energy Measurement.—This was done by means of either a 1-cm. or a 2-cm. Moll thermopile (previously calibrated against a standard Hefner candle), the *E.M.F.* generated being measured by means of a potentiometer (Cambridge Instrument Company) and a moving-coil galvanometer (Gambrell). The over-all sensitivity was about 5×10^{-7} volt. Care was naturally taken that the whole of the beam under measurement fell directly on the surface of the thermopile, and all necessary corrections were applied for reflexion losses at the different quartz–air and quartz–liquid surfaces. Measurements of incident energy made at the beginning and end of any reaction usually agreed to within 1—2%. Measurement of the absorbed energy during the reaction proved to be undesirable for various practical reasons, one of which was the effect of intermittent illumination (*q.v.*). Consequently, the absorbed energy, though sometimes determined at the end of a reaction, was usually calculated.

Intensity Variation.—This was normally effected by altering the size of the aperture in the diaphragm F (Fig. 2) or the position of the lens C_2. The beam being convergent, the intensity was smaller the closer the lens to the cell and thermopile. In some cases, the average, as opposed to the true, intensity was varied by the use of an electrically driven rotating sector of variable aperture, running at a high speed (20—25 interruptions per sec.) and placed close to the aperture F, between it and C_2.

Variation of Duration of Insolation.—As it was found that, under certain conditions, the rate of the photolysis was proportional to the square root of the light intensity, it became desirable to carry out experiments under conditions of slowly intermitted radiation. The same sector, rotating with constant aperture, was used for this purpose, its rate of rotation being controlled by a simple gearing interposed between sector and motor, and consisting of six two-step pulleys rotating freely on one of two parallel stationary axes, and coupled with one another by suitable belting. The radii of the two steps in each pulley were in the ratio of 4 : 1. By changing the number of pulleys in use and suitably connecting them together, the sector speed could thus be varied between the extremes of 1/4 and 1/4000 of the speed resulting when motor and sector were directly coupled together. Alteration of the speed of the motor by a series resistance allowed of finer adjustments. In actual use, the maximum duration of a single light-period was 100 secs. In these experiments, the diaphragm F, with its immediately adjacent sector, and the reaction cell G were so arranged as to be at conjugate foci of the lens C_2. This ensured that, at any particular point in the photolyte, the cut-off or switch-in of the light intensity was sudden and not gradual.

Concentration Variation.—Starting with the most concentrated solution, this was carried out by one of two methods, *viz.*, (i) replacement of some of the solution in the cell by distilled water; (ii) decomposition of some of the peroxide by insolation. The water used was made from ordinary laboratory distilled water by redistilling it from alkaline permanganate, passing the steam successively through a hot solution of potassium hydrogen sulphate, a 6-inch column of glass wool, and two trap-bulbs, and finally condensing it in a silica condenser and storing in a large waxed glass flask, sealed with a waxed glass plate. When the second method of dilution was used, the reaction cell was simply placed a few inches in front of the unscreened mercury arc and insolated for 24—48 hours. As already mentioned, this had the effect of destroying the fluorescent impurity in the perhydrol.

The concentrations of the various solutions were determined by titration with permanganate. For concentrated solutions, a 1-c.c. silica pipette was used and N-potassium permanganate; for the more dilute solutions, heavily waxed glass pipettes and permanganate solutions as dilute as $0{\cdot}01N$ were employed. All concentrations are expressed as g.-mols. of hydrogen peroxide per litre.

Temperature Coefficients.—These were measured by carrying out a series of determinations with the thermostat adjusted at various temperatures from 2° to 26°, the limits being determined by the magnitude of the thermal reaction with the particular peroxide solution under examination. In order to avoid condensation of moisture on the surface of the front quartz window of the thermostat during measurements at low temperatures, a wide tube about 3″ long, containing a small amount of phosphoric oxide and closed by a quartz plate, was firmly cemented on the front surface of the thermostat. This effectually prevented any condensation trouble.

Experiments with Dilute Solutions.—Several such series were studied. With the full light of the lamp, or chlorine-filtered light, a cell was used consisting of quartz plates sealed on by paraffin wax to a glass frame 5 mm. thick, through which a circular central cavity had been cut. The internal glass surface of this cavity was coated with paraffin wax, and a hole drilled into it from the edge of the frame allowed of filling and withdrawing of samples for titration. When 365 $\mu\mu$ light was used, in order to shorten the experiment, the cell consisted of a small quartz flask immersed in a metal box, through which a rapid stream of tap water flowed, provided on opposite sides with windows consisting of plates of Corning Glass G. 586 A.W. (see p. 602). A mercury arc was placed 10 cm. away from either window, and thus a reasonable rate of decomposition was secured. The reaction was followed in one case by titration, in others by measuring the oxygen given off under atmospheric pressure conditions. The latter procedure was capable of a fair degree of accuracy, as the runs were long, owing to the small amount of light absorbed, and the degree of supersaturation of oxygen could be kept so low as not to affect the results appreciably. In all cases where titration methods were used, the upper portion of the cell was blackened over, so that the surface insolated might remain constant throughout the run.

UNIVERSITY OF LONDON,
KING'S COLLEGE.

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