
CCCLXXIX.—*The Photochemical Decomposition of Aqueous Oxalic Acid Solutions.*

By Arthur John Allmand and Lewis Reeve.

A certain amount of work has already been done on the photolysis of oxalic acid. The decomposition of the solid was first noted by Berthelot and Gaudechon (*Compt. rend.*, 1911, **152**, 262), using the full light of a quartz–mercury lamp placed a few cm. from the oxalic acid contained in a quartz tube over mercury. The production of carbon dioxide and of formic acid is the first result, the latter substance undergoing further decomposition with liberation of more carbon dioxide, and of carbon monoxide, hydrogen, and methane (*ibid.*, 1910, **151**, 478). In a subsequent paper (*ibid.*, 1914, **158**, 1791) they reported that sunlight, acting for 3 months on the solid acid (in quartz), had no visible action, and concluded that wave-lengths shorter than 300 μμ were necessary for the decomposition. Further experiments with the quartz lamp confirmed their first results—the products were formic acid and a gaseous mixture of composition CO_2, 87; CO, 9·5; H_2, 3·5%. The reaction has also been investigated by Noyes and Kouperman (*J. Amer. Chem. Soc.*, 1923, **45**, 1398), more particularly from the point of view of the kinetics of the reaction and of the effect of wave-length. They found that the shorter the latter the more rapid the reaction. Wave-lengths longer than 250 μμ were inactive. Large induction periods were noticed, and water was shown to be a positive catalyst. The hydrated acid decomposed far more rapidly than the anhydrous substance.

Berthelot and Gaudechon (*Compt. rend.*, 1914, **158**, 1791) were also the first to work on the photolysis of the aqueous solution. Just as with the solid acid, continued exposure to sunlight was without effect. Insolation by the quartz–mercury lamp with interposition of a glass screen 0·14 mm. thick (cutting off rays below 250 μμ) caused slow decomposition of an 8% solution, with production of formic acid and a gaseous mixture of composition CO_2, 88—90; CO, 10—12%. The quantity of gas collected never exceeded 1 c.c. When experiments were carried out in the absence of the glass screen, the results were different. After 90 minutes' exposure, formic acid could be detected in the solution, and the composition of the gases was CO_2, 62; CO, 10; H_2, 28%; but after 16 hours' exposure neither formic acid nor carbon monoxide was present, the gases consisting of CO_2, 67; H_2, 33% (greater in volume than after the shorter exposure, but by no means increased in proportion to the longer time). Further prolonged insolation merely resulted in increasing the quantity of gas produced, but left its composition unchanged. Traces of formaldehyde were at the same time found in the liquid. The production of formaldehyde and, in addition, of reducing sugars was also noticed in this photolysis by Baly, Heilbron, and Barker (J., 1921, **119**, 1025) as a result of 40 hours' insolation of a saturated solution by a quartz–mercury lamp.

The conclusions of Berthelot and Gaudechon were, briefly, (*a*) that the fundamental reaction in the photo-decomposition of aqueous oxalic acid sets in below 300 μμ and is $H_2C_2O_4 \longrightarrow CO_2 + H\cdot CO_2H$; (*b*) that, in the wave-length region 300—250 μμ (middle ultra-violet), the formic acid produced undergoes a secondary decomposition $H\cdot CO_2H \longrightarrow H_2O + CO$; and (*c*) that, below 250 μμ (extreme ultra-violet), the secondary decomposition $H\cdot CO_2H \longrightarrow CO_2 + H_2$ takes place, and, moreover, completely—so that in light of this spectral region oxalic acid is decomposed according to the total equation $H_2C_2O_4 \longrightarrow H_2 + 2CO_2$. No explanation is given as to what happens during long exposures in the complete light of the lamp to the carbon monoxide which is formed during the first few hours and which they consider to be the result of the photo-decomposition of formic acid by light of wave-length 250—300 μμ. Light of this wave-length, it may be remarked, was present throughout the 16-hour run referred to above, during which the previously-formed carbon monoxide disappeared.

Our experiments were commenced with the two purposes of investigating the reaction quantitatively from the point of view of energetics and of examining the mechanism proposed by Berthelot and Gaudechon with a view to clearing up certain discrepancies, of which that quoted above is the most striking. The work proved difficult, and more than 2 years were required to get definitive results. Since it was finished (in May 1923), papers dealing with the subject have been published by Volmar (*Compt. rend.*, 1925, **180**, 1172; see also *ibid.*, 1924, **178**, 697) and by Anderson and Robinson (*J. Amer. Chem. Soc.*, 1925, **47**, 718). Volmar attempted to calculate the threshold frequency necessary for the photolysis of oxalic acid solutions by equating the heat of decomposition of a molecule of the acid to the size of the quantum which would just suffice to break it up. He obtained wave-lengths of 320 μμ for decomposition according to the equation $H_2C_2O_4 \longrightarrow CO_2 + H\cdot CO_2H$, and 210 μμ for the secondary reaction $H\cdot CO_2H \longrightarrow CO_2 + H_2$. Hydrogen should therefore only be a product of oxalic acid photolysis when working with very short wave-lengths, and this agreed with the results of Berthelot and Gaudechon. Volmar did not attempt to deal with the reported formation of carbon monoxide. Anderson and Robinson insolated a 0·1*N*-solution with the total light of a quartz–mercury lamp, following the reaction by titration with potassium permanganate solution, and measuring the absorbed light by a thermopile–galvanometer combination. Assuming the average size of the absorbed quanta to be 7×10^{-12} erg (corresponding to a wave-length of about 283 μμ), they calculated an average quantum efficiency of 1/1392 for the whole spectral region.

Preliminary Experiments.

It was recognised at the commencement of the work that following the reaction by titration methods would be unlikely to give accurate results. The decomposition is slow, and the products of reaction formic acid and perhaps formaldehyde, are difficult of estimation in the presence of a large excess of oxalic acid. In any case, the nature and the proportions of the gaseous products were matters of primary interest, and it was decided at the outset to concentrate on their investigation and estimation. It soon became evident that there was no possibility of quantitative results when working at atmospheric pressure, owing to gaseous supersaturation. It was also established that the rate of evolution of gas was of the order of 0·1 c.c. per hour with the cell then in use in the full light of a quartz–mercury lamp (iron and carbon arcs were even less effective). It was therefore clear (*a*) that the gases would have to be removed by evacuating the insolated solution, and (*b*) that some form of micro-gas technique would have to be employed for their measurement and analysis.

Apparatus 1, in which insolation cell and capillary measuring tube were fused together, and apparatus 2, in which the evolved gases were swept out through greased taps by mercury, both failed, owing, respectively, to the impossibility of adequate preliminary evacuation and to the gas becoming trapped by greasy mercury. These difficulties were surmounted as follows. The two photochemical cells employed were circular in cross-section, of glass, and with plane ends of polished quartz cemented on. Both were 5 cm. deep, their respective internal diameters being 5 and 7·5 cm., and their volumes 98 and 221 c.c. When in use, connexion was made by means of a side-tube and a mercury-sealed ground joint with a mercury-sealed three-way tap, and then, through a phosphorus pentoxide tube, with a Toepler pump. The larger cell had, cemented on its front, a 1 cm. quartz–water cell to absorb the heat rays. The Toepler pump was of the ordinary pattern, except that the usual ground-glass, mercury-tight valve was absent. In its place, the side-tube connecting with the photochemical cell was continued vertically upwards for such a distance that, when discharging the gaseous contents of the barrel into the gas-delivery pipette, no mercury could pass back into the apparatus. The purpose of this change was to avoid possible trapping of bubbles at the ground-glass surfaces. The gases were collected and transferred by means of the usual technique (see Travers, “ Study of Gases ”). With this apparatus (apparatus 3), working in the way presently to be described, results satisfactory within limits were obtained, casual losses of gas being practically eliminated.

The measurement and analysis of the gases were carried out by methods which have already been described (Reeve, J., 1924, **125**, 1946). It need only be mentioned here that the technique finally developed allowed of measurements of volume with an absolute accuracy of about 0·0002 c.c., the volume of a single division in the capillary measuring tube employed being 0·000547 c.c. As will be seen, the samples of gas dealt with in the course of the work differed very much in volume, but were generally of the order of 100 divisions, *i.e.*, 0·05 c.c. When fully developed, the analytical methods used for carbon dioxide (absorption by solidified fused potassium hydroxide), hydrogen, and carbon monoxide (explosion with oxygen at ordinary or reduced pressure) enabled us, we estimate, to determine the quantities of these gases present to about the same absolute accuracy as in the total volume measurement. At the stage of the work now being described, however, the methods of dealing with very small amounts of hydrogen and carbon monoxide had not been worked out.

Results with Apparatus 3.

Experiment 1. The smaller cell (98 c.c. capacity) was charged with 90 c.c. of 0·097M-oxalic acid and the apparatus evacuated by the Toepler pump, the tap connecting the cell with the pump being occasionally opened for a short interval and then closed. The final traces of air were difficult to remove, and *two weeks* of pumping were found necessary for the purpose. The amount of water lost by evaporation only affected the concentration to a fraction of 1%. Insolation was then started, using the full light of a 110-volt quartz–mercury lamp, placed at the focus of a quartz condenser lens, and with a quartz–water cell stationed between the lens and the photochemical cell in order to cut out the heat rays. After 5 hours' insolation, the lamp was switched off, and the gases produced (almost entirely still dissolved in the solution) were pumped off. It was found impossible in practice to remove them completely, the last traces being held with great tenacity. Instead of this, the cell was opened to the pump and shut off again for a definite number of times (usually four), cell and pump remaining in connexion with one another for 15 seconds on each occasion. Another 5 hours' insolation was given, and the same procedure repeated. After the first few treatments of this kind, it was found that the same amount of gas, of the same composition, was pumped off after each insolation. We concluded that, in consequence of our uniform procedure, the same conditions with regard to gas saturation were being reproduced after each quadruple evacuation, and, therefore, that the gases collected in this manner actually represented the decomposition brought about by the light during the previous exposure.

The results obtained after conditions had become constant are given below (volumes expressed as divisions, *i.e.*, 0·000547 c.c.). The time of insolation was 5 hours in each case.

Total vol. of gas.	Vol. of CO_2.	Vol. of CO.	Residue.
146	130	5·5	10·5
150	133·5	5	11·5
147	130	7·5	9·5
150	137	—	—

Considering the nature of the work, the degree of reproducibility must be considered good. Although the residual gas samples, after absorption of the carbon dioxide, were exploded with oxygen, the technique of working with these small quantities had not been fully developed, and consequently no figure can be quoted for the quantity of hydrogen present. The amount of carbon monoxide could, however, be calculated from the diminution in volume observed on treatment with potash after the explosion. The greater part of the residue (col. 4) was probably air (leakage during the experiment or unremoved during the preliminary evacuation).

Experiment 2. The larger cell (221 c.c. capacity) was used, filled with 0·5*M*-oxalic acid, and another lamp employed, of rather different energy distribution. The preliminary evacuation took well over *three weeks*. In order to get an idea of the proportion of hydrogen present in the gas, the residues (after carbon-dioxide absorption) from a number of the separate insolations were collected together, and the whole was analysed for carbon monoxide and hydrogen. Below are given results of *all* the separate 3-hour insolations, including those made before constant conditions had been reached (volumes of gas in " divisions " as before).

Total vol. of gas	—	217	228	234	247	266	252	249
Vol. of CO_2	189	195	207·5	—	226	247	238	235

The vols. of CO and H_2 were 8 and 3·5 respectively (average of collected samples).

It will be seen that, again, after the first few insolations, the volume of gas (and its percentage of carbon dioxide) produced by a 3-hour exposure became practically constant, the experimental error being of the order of 5%. This error is due rather to imperfections in the method of collection or to inconstancy in the light source than to errors in measurement or analysis, which are certainly less than 1%. The small residue unaccounted for apparently decreased during the course of the experiment, and probably was due to air unremoved at the start.

These two experiments demonstrated that, under constant conditions (the concentration of the oxalic acid of course hardly altered during an experiment), the rate of decomposition was constant—a result to be anticipated, but nevertheless valuable as showing to what extent the experimental technique could be relied on. They also, however, made clear the necessity of modifying the latter in such a way as to eliminate the weeks of preliminary evacuation, and so permit of more rapid working. As experience had shown that the larger the volume of solution the longer the time required for evacuation, it was obviously desirable to reduce the size of the cell as much as possible. Consequently, a cell of similar construction to those hitherto used, but of only 2·5 cm. internal diameter, was made up; its volume was about 24·5 c.c. Further, in order to increase the uniformity of the so-called "parallel" beam of light employed, and so make it possible to determine its total energy flux more exactly, the mercury lamp was fitted with a diaphragm provided with a circular aperture (several were used on different occasions, their diameters being 1·0, 1·4, and 1·8 cm.; most measurements were done with 1·4 cm.). At the same time, in order to increase the intensity of the incident light, and thus bring about a total decomposition of about the same order as before, the parallel beam was passed through a second quartz condenser, thereby being turned into a convergent beam directed on to the front of the cell, and brought to a focus about half-way through the oxalic acid solution. These changes (the whole as modified constituting apparatus 4) were successful. The time required for complete preliminary evacuation was reduced to 2—3 days (the increase in concentration owing to loss of water was about 0·25%), and, moreover, it was found possible to pump off completely the gaseous products of photolysis after exposure, and thus to eliminate one uncertain source of error. Naturally, in order to get reproducible results during the insolation, very great care had to be taken to have cell, lenses, and lamp in precisely the same relative positions during every exposure.

Results with Apparatus 4.

It was first of all necessary to test the proportionality between extent of reaction and time of exposure with the new experimental arrangement. This was done as follows.

Experiment 3. A solution of oxalic acid was exposed for 23·75 hours. The gaseous products (in divisions) were: CO_2, 297; CO, 7; H_2, undetermined. It was then re-exposed for 7 hours, and there were produced: CO_2, 95; CO, 2; H_2, 1. Assuming a constant rate of reaction, the 7-hour exposure should have given: CO_2, 87·6; CO, 2. As it was thought that a slight shift in the apparatus had taken place between the two exposures, thus causing the discrepancy in the carbon dioxide value, the experiment was repeated.

Experiment 4.

	Found for 17·7 hrs.	Calc. for 7·5 hrs.	Found for 7·5 hrs.
CO_2	226·5	96	94
CO	4·0	1·7	1·8
H_2	4·4	1·9	1·8

The agreement is satisfactory.*

We then directed our attention to the effect of wave-length.

Experiment 5. A 0·68*M*-solution of oxalic acid was insolated for a considerable period by a beam which had passed through a filter consisting of 5 mm. of a 0·2% aqueous quinine sulphate solution, and was therefore free from ultra-violet light. No perceptible decomposition resulted. This was to be expected, as oxalic acid shows no absorption in the visible region. It is nevertheless evidence that the material used was free from traces of such impurities as iron, which are known to sensitise its photolysis in visible light. It may be mentioned that 10 g. of the acid, on incineration, left no visible residue.

Experiment 6. According to Berthelot and Gaudechon, oxalic acid solutions are not affected by light of wave-length longer than 300 μμ. As, however, their technique was clearly not capable of detecting such small amounts of decomposition as ours, and as our measurements (quoted later) had shown oxalic acid solutions to absorb appreciably at 365 μμ, we insolated the same 0·68*M*-solution in quartz–mercury light which had passed a filter consisting of 5 mm. of 0·075% solution of Casella's Diamond Fuchsin (large crystals), held between quartz plates. This cell replaced the water cell used in Expts. 1—4. The solution has been shown in this laboratory to pass 30% of the incident 365 μμ radiation, about 1·2% of both the 313 μμ and the 405 μμ lines, and otherwise nothing except in the red. The result of 25 hours' insolation was the production of 4·5 divisions of gas, all carbon dioxide within the limits of accuracy of our technique. Carbon monoxide and hydrogen, if present in the same proportions as in previous insolations, would have been undetectable. This quantity of gas, although small, undoubtedly represents a real decomposition, and we therefore conclude that oxalic acid solutions are photosensitive to light of wave-length 365 μμ. (This and the next few experiments were

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* When determining carbon monoxide and hydrogen in the gaseous residue left after absorbing carbon dioxide, the residue in this and in subsequent experiments was given a preliminary sparking *before* adding oxygen. This point is of importance and will be discussed later.

carried out under conditions which enabled the subsequent calculation of quantum efficiencies.)

The next point of interest was to determine whether the proportions of hydrogen and carbon monoxide in the products of decomposition altered with wave-length. According to Berthelot and Gaudechon, this is the case, carbon monoxide being a secondary product of decomposition between 300 and 250 μμ, and hydrogen below 250 μμ.

Experiment 7. A 0·62*M*-solution was exposed for 28 hours behind a filter (in quartz) of 5 mm. of 0·0125% Auramin O (no water cell employed). Measurements in this laboratory have shown that such a solution transmits thus :

254 μμ	Nil.	297 μμ	0·40
265	Possible trace.	303	0·368
280	0·251	313	0·263
290	0·364	365	Nil.

The volumes of gas obtained were CO_2, 73·5 divs.; CO and H_2, each 1·5 div. An exposure to the full light of the lamp at that time gave, per 73·5 divs. of CO_2, 1·3 divs. CO and 1·4 divs. H_2, *i.e.*, the same proportions within experimental error.

Experiment 8. A 0·62*M*-solution was then exposed for 22·8 hrs. behind a filter consisting of 1 cm. of chlorine at atmospheric pressure between quartz plates. The quartz–water cell was used in addition. The transmission of the complete filter in the ultra-violet region (more accurate data have since been obtained) was determined approximately as :

248 μμ	0·50	270 μμ	0·50	290 μμ	0·15	313 μμ	0·035
254	0·50	275	0·45	297	0·12	334	0·085
265	0·50	280	0·40	303	0·11	365	0·13

It may be mentioned that a cement containing pitch had been used for attaching the quartz plates to the hollow glass block employed in the construction of this filter. Although chlorine gas was passed through for 2 days before sealing the filter off, and the transmission remained apparently unchanged over a period of 2 months, it is probable that vapours of some chlorinated material present were the cause of the discrepancies found between the observed transmissions and those of a pure chlorine filter.

The resultant gases were CO_2, 70 divs.; CO, 5 divs.; H_2, 4 divs. Under the same conditions with the total light of the lamp, about 1·3 divs. of each of carbon monoxide and hydrogen would have been obtained per 70 divs. of carbon dioxide. The effect of decreasing the average incident wave-length is thus to increase very considerably the proportion of gases other than carbon dioxide resulting from the photolysis. When the impure nature of the light passed by the chlorine filter is taken into account, the relative increase is even greater than appears from the above data. On the other hand, there is no sign of any variation in the proportions of carbon monoxide and hydrogen with change in frequency, as was found by Berthelot and Gaudechon.

Mechanism of the Reaction.

In discussing these results, it must be remembered that they hold for the *initial* stages in the photolysis of oxalic acid solutions —in no case was more than a very small fraction of the acid decomposed. It was therefore not likely that the carbon monoxide and hydrogen arose by secondary photo-decomposition of the traces of primarily-produced formic acid, and this view was confirmed by later work on the quantum efficiency of formic acid decomposition (see following paper) combined with a knowledge of the extinction coefficients of the two acids. In any case, however, the production *both* of carbon dioxide *and* of the other gases has been shown to proceed at a constant rate, independent of the extent of decomposition (which was in its initial stages). But if carbon monoxide and hydrogen resulted from a secondary photo-decomposition, then the amounts produced should clearly be proportional to the *square* of the time, in consequence of the continually increasing formic acid concentration.

A possible explanation is that definite fractions of the oxalic acid molecules decompose directly on absorption of light according to the equations

$$(a)\ H_2C_2O_4 \longrightarrow 2CO_2 + H_2,$$
$$(b)\ H_2C_2O_4 \longrightarrow CO_2 + CO + H_2O,$$

or, which amounts to practically the same thing, that definite fractions of the primarily-produced formic acid molecules have particularly high energy contents at their instant of formation, and decompose further in accordance with the equations

$$(a)\ H{\cdot}CO_2H' \longrightarrow H_2 + CO_2,$$
$$(b)\ H{\cdot}CO_2H' \longrightarrow H_2O + CO.$$

Such assumptions would explain the constant rate of production of hydrogen and carbon monoxide, but, in order to account for the relative proportions in which they appear, it would be necessary to assume further that the probabilities of the reactions (*a*) and (*b*) are of the same order.

Another possibility, however, suggested itself. It is well known that formaldehyde results in many cases when organic substances are exposed to ultra-violet light, including sunlight (*e.g.*, Moore and Webster, *Proc. Roy. Soc.*, 1918, *B*, **90**, 168; Baly, Heilbron, and

Barker, *loc. cit.*; Dhar and Sanyal, *J. Physical Chem.*, 1925, **29**, 926). In particular, the production of formaldehyde in this reaction had been reported by Berthelot. One could imagine it to be formed by interaction between nascent or "activated" carbon dioxide molecules of high energy content and water, in accordance with the equation $CO_2' + H_2O \longrightarrow H{\cdot}CHO + O_2$, as was suggested by Baly, Heilbron, and Barker (who also remarked its occurrence as a product of the present reaction). If it were actually present, but undetected, it would behave when subjected to analysis by our methods as a mixture of carbon monoxide and hydrogen—and, moreover, 1 vol. of formaldehyde vapour would behave like a mixture of 1 vol. of carbon monoxide plus $\frac{1}{3}$ vol. of hydrogen. For, on explosion with oxygen, we should have, in the one case

$$\text{Residue} + \underbrace{H{\cdot}CHO + O_2}_{\text{2 vols.}} \longrightarrow \underbrace{H_2O + CO_2}_{\text{1 vol.}} + \text{Residue},$$

and, in the other,

$$\text{Residue} + \underbrace{CO + \frac{1}{3}H_2 + \frac{2}{3}O_2}_{\text{2 vols.}} \longrightarrow \underbrace{\frac{1}{3}H_2O + CO_2}_{\text{1 vol.}} + \text{Residue},$$

i.e., in either event, the contraction, both after explosion and also after subsequent treatment with potash, would be 1 vol. If, on the other hand, a gaseous mixture, free from hydrogen and carbon monoxide but containing formaldehyde, were sparked beforehand, there should be an increase in volume corresponding to the equation $H{\cdot}CHO \longrightarrow H_2 + CO$, and, on subsequent combustion with oxygen, the ratio $H_2 : CO$ found should be 1 : 1, and the absolute volume of either gas would be equal to the volume of formaldehyde present in the original mixture.

After the possibility of accounting in this way for the apparent hydrogen and carbon monoxide contents of the products of photolysis had occurred to us, the gaseous residues, after removal of carbon dioxide, were sparked before adding oxygen and exploding. The result was *always* an increase in volume, equal, within experimental error, to the absolute amounts of *either* hydrogen *or* carbon monoxide found during the subsequent analysis. The residues from Expts. 4, 7, and 8 were treated in this way, with the following results (volumes in divisions):

Expt. No.	Increase in vol. on sparking.	Vol. of CO.	Vol. of H_2.
4	4·0	4·0	4·4
7	1·5	1·5	1·5
8	5	5	4

On the other hand, in those experiments (2 and 3) in which the explosion with oxygen was carried out without a preliminary sparking of the gas, the ratios $CO : H_2$ found were 2·3 : 1 and 2 : 1, respectively. When the minute quantities of gas dealt with are remembered, the discrepancy between these figures and the ratio 3 : 1 is not surprising.

To confirm the probable conclusion that what we had originally taken for a mixture of carbon monoxide and hydrogen was really formaldehyde, this substance was tested for in solutions of oxalic acid which had been exposed to light, but not subsequently evacuated. None was found when using apparatus 4, even after a 26-hour exposure of a $0{\cdot}7M$-solution. Nor was a positive result anticipated, assuming that the total amount formed corresponded to the quantity pumped off and detected by our method of gas analysis, as it would lie outside the limits of sensitivity of the Buchanan–Schryver test employed. When, however, an identical solution was exposed in a quartz test-tube to the full light of the quartz–mercury lamp at a distance of 7 cm., a distinct positive test was obtained.

One further point may be mentioned. We have suggested a mechanism of formaldehyde formation which involves the simultaneous production of oxygen, molecule for molecule; and it might be asked why, this being the case, when the residues were given their preliminary sparking, the reaction $H{\cdot}CHO + O_2 \longrightarrow H_2O + CO_2$ did not take place. In this connexion, it must be remembered (1) that the photolysis products, after removal of carbon dioxide, contained an excess of residual gas, probably air, (2) that the sparking was carried out at reduced pressure (Reeve, *loc. cit.*, pp. 1951, 1952), and (3) that the sparking bulb had a maximum diameter of only 2—3 mm. All these factors would tend to limit the explosion range, and, taken together, are enough to account for inhibition of the explosion. The *dissociation* of formaldehyde on sparking would not be affected in the same way. It is a unimolecular reaction, and, if regarded as a purely thermal one, is known to take place at a low temperature. Of course, other mechanisms of formaldehyde formation are conceivable. Thus, a small fraction of the oxalic acid molecules might decompose in accordance with the equation $H_2C_2O_4 \longrightarrow 2CO_2 + H_2'$, the activated hydrogen then reacting further as follows: $H_2' + H_2C_2O_4 \longrightarrow CO_2 + H_2O + H{\cdot}CHO$. We consider an analogous mechanism in the succeeding paper, and the suggestion is one which could be tested in an obvious manner. The fact that, using a *saturated* oxalic acid solution, Baly, Heilbron, and Barker noted the formation, not only of formaldehyde, but also of reducing sugars, is perhaps significant. On the whole, however, whilst recognising this possibility, we prefer the first mechanism proposed. It is simpler, and has the advantage of accounting for the production of formaldehyde during other organic photolyses.

Our conclusions regarding the mechanism of this photo-decomposition are seen to differ considerably from those arrived at by Berthelot and Gaudechon, who, however, carried the degree of decomposition of their oxalic acid solutions much farther than we did. As it was possible that the increasing accumulation of formic acid in these circumstances might affect the reaction, we took up the subject of the photolysis of this acid, and our results are contained in the next paper.

Energetics of the Reaction.

Expt. 6 and later ones were carried out using beams of light of measured total intensity and spectral energy distribution, thereby making possible the calculation of quantum efficiencies (see, however, later). The total visible and ultra-violet energy in the beam was determined after it had passed the first quartz condenser lens and a 2 cm. quartz–water filter, but before it had been concentrated on to the cell by the second quartz condenser. This was done by means of a Coblentz thermopile and a Broca galvanometer. The distribution of energy over the area of the beam was by no means uniform, and necessitated the taking of a large number of systematic measurements, and averaging the results. The readings thus obtained were converted into absolute units by measuring the deflexion given by the same thermopile combined with a Paschen galvanometer when irradiated by a standard Hefner lamp at 1 m. distance. The sensitivities of the two galvanometers were carefully measured and their slightly differing resistances taken into account. Two lamps were used, the aperture of the diaphragm covering them being 1·4 cm. in every case. The results found for the average total visible and ultra-violet energy under these conditions were:

Lamp 1. 17·73 *H.K.* or 16750 ergs/cm.^{2}/sec.
Lamp 2. 14·03 *H.K.* or 13240 ergs/cm.^{2}/sec.

To get the total energy entering the cell per second, these figures were multiplied by 41·7 × 0·9 × 0·95, representing, respectively, the effective area of the second (concentrating) lens, and corrections for the reflexion losses at the surface of this lens and at the front surface of the cell. The method of measuring the spectral energy distribution in the beams used has been described elsewhere (Franklin, Maddison, and Reeve, *J. Physical Chem.*, 1925, **29**, 713). The final figures obtained with lamp 1 can be applied with some confidence. In the case of lamp 2, some time elapsed between these determinations and certain of the experiments, thus introducing an uncertain error, which we estimate as being of the order of 10%.

Fresh measurements were made of the extinction coefficients of oxalic acid solutions, using a quartz spectrometer, Coblentz thermopile and Paschen galvanometer. The results, where k (the molecular extinction coefficient) is given by $(1/cd)\log_{10} I_0/I$ (c in g.-mols. per litre, d in cm.), were as follows :

λ.	k.	λ.	k.	λ.	k.	λ.	k.
365 μμ	0·0155	303 μμ	1·57	280 μμ	11·3	265 μμ	36
334	0·11	297	2·2	275	21	254	54
313	0·19	290	4·8	270	26	248	58

Bielecki and Henri (*Compt. rend.*, 1912, **155**, 456) give the following values :

λ in μμ	300	290	269·3	266·5	255	245·2
k	2·2	4·8	24·6	32	54	61

Beer's law was shown to hold, at least approximately, between concentration limits of 0·5—0·1M for 313 μμ and 0·5—0·01M for 303 μμ. For other wave-lengths, the absorption was either too strong or too weak for this law to be tested. The figures for 297 μμ and shorter wave-lengths were obtained with 5 cm. and 5 mm. layers of a 0·01M-solution.

The details of the calculation of quantum efficiency are given for one simple case only.

Quantum Efficiency for 365 μμ. This was calculated from the results of Expt. 6, neglecting the very slight absorption of active wave-lengths other than 365 μμ. The data were :

Lamp used	No. 1.	k	0·0155.
Duration of expt.	25 × 3600 secs.	Depth of cell	5 cm.
Conc. of oxalic acid ...	0·68M.	Fraction of 365 μμ absorbed	0·114.

Ergs of λ 365 μμ passing water cell $= a = 3270/\text{cm.}^2/\text{sec.}$

Ergs of λ 365 μμ passing filter cell $= b = a \times 0{\cdot}30/\text{cm.}^2/\text{sec.}$

Ergs of λ 365 μμ entering photo-chemical cell $= c = b \times 0{\cdot}9 \times 0{\cdot}95 \times 41{\cdot}7/\text{sec.}$

Ergs of λ 365 μμ absorbed by oxalic acid $= d = c \times 0{\cdot}114/\text{sec.}$

Ergs of λ 365 μμ absorbed by oxalic acid in course of run $= e = d \times 25 \times 3600.$

Quanta of λ 365 μμ absorbed by oxalic acid in course of run $= e \times 10^{13} \div 54.$
$= 6{\cdot}64 \times 10^{19}.$

Carbon dioxide formed = 4·5 divisions at 15°.
= 4·2 divisions at *N.T.P.*
= 4·2 × 0·00055 c.c. at *N.T.P.*
$= 4{\cdot}2 \times 0{\cdot}00055 \times 6{\cdot}1 \times 10^{23} \div 22{,}400$ molecules
$= 6{\cdot}29 \times 10^{16}$ molecules.

Hence quanta absorbed/molecules decomposed = 1060 for 365 μμ.

Quantum Efficiency for 300 μμ. This was determined from the results of Expt. 7, carried out with lamp 2, and with a filter passing light of wave-lengths 280—313 μμ in proportions already given. The quantities of energy absorbed by the oxalic acid per second for the different components of the radiation were calculated from the spectral energy distribution in the beam, the transmission of the Auramin O filter, and the extinction coefficients of the solution. Absorption was complete up to 303 μμ, and the centre of gravity of the absorbed energy under those conditions lay at about this wave-length. The total number of quanta of mean value 66×10^{-13} ergs absorbed in the 28-hour run was $2{\cdot}625 \times 10^{20}$ and the number of molecules of oxalic acid decomposed, allowance being made for the amount represented by the formaldehyde, was $1{\cdot}07 \times 10^{18}$. Hence, quanta absorbed per molecule decomposed = 245 for 300 μμ.

Quantum Efficiency for 265 μμ. The results of Expt. 8 are utilised for this calculation. As the chlorine filter employed passed large quantities of light elsewhere than between 254 and 275 μμ, of which region 265 μμ was taken as the typical wave-length, the results obtained must be corrected by means of the quantum efficiencies previously determined. (The actual amounts of light absorbed by the oxalic acid for the different spectral regions stood in the ratio 334—365 μμ : 280—313 μμ : 254—275 μμ = 1 : 4·67 : 5·83.) The total number of molecules of oxalic acid decomposed was $10{\cdot}64 \times 10^{17}$. Of these, $0{\cdot}164 \times 10^{17}$ and $2{\cdot}834 \times 10^{17}$ have been calculated as having been decomposed by 365 μμ and the 300 μμ group, respectively. This leaves $7{\cdot}64 \times 10^{17}$ molecules as the share of the 265 μμ group, of which the number of absorbed quanta was calculated as $7{\cdot}65 \times 10^{19}$. Therefore, quanta absorbed per molecule decomposed = 100 for 265 μμ.

It was thought desirable to check these results by means of an experiment done with the whole light of the lamp.

Experiment 9. A 0·68*M*-oxalic acid solution was insolated for 7 hours, merely using a water filter. After correction for loss as formaldehyde and for temperature, the result was the formation of 0·092 c.c. of carbon dioxide at *N.T.P.*, *i.e.*, of $2{\cdot}50 \times 10^{18}$ molecules. The absorbed quanta were calculated as previously, the results being given below, together with the theoretical number of molecules decomposed, assuming the correctness of the above quantum efficiencies :

λ (in μμ).	Ergs absorbed.	Quanta absorbed.	Calc. decomp. (molecules).
248·5—275	$8{\cdot}67 \times 10^8$	$1{\cdot}16 \times 10^{20}$	$1{\cdot}16 \times 10^{18}$
280 —313	28·7	4·35	1·78
334 —365	3·86	0·71	0·07

The total calculated decomposition is thus $3{\cdot}01 \times 10^{18}$ molecules, Considering the nature of the experiments and the uncertain factor with regard to lamp 2 already noted, the agreement with the experimental value of $2{\cdot}50 \times 10^{18}$ is sufficiently good.

We can therefore summarise the efficiency results for a 0·6—0·7*M*-solution as follows :

λ (in μμ).	Quanta/molecule.	Quantum efficiency (γ).
265	100	0·01
300	245	0·0041
365	1060	0·00094

The relative values of γ are as generally found—an increase in frequency results in an increased probability of decomposition following on quantum absorption. According to Anderson and Robinson (*loc. cit.*), the average quantum efficiency for the decomposition of a 0·05*M*-oxalic acid solution in the full light of the quartz–mercury lamp is only 1/1392. They estimated the average size of their absorbed quanta as 7×10^{-12} ergs, which corresponds to a wave-length of about 283 μμ, for which our results point to a value of γ of about 1/160. We can only conclude, from the fact that these authors were estimating the amount of decomposition by titration with potassium permanganate, that they were under the impression that the decomposition taking place was identical with the most important of the reactions which occur in the presence of uranyl salts, *viz.*, $H_2C_2O_4 \longrightarrow H_2O + CO + CO_2$.

Actually, however, the permanganate titre of their solution would remain constant or diminish very slightly, depending on the exact method of carrying out the titrations, and this would account for the very low quantum efficiency observed.

It may be pointed out that the literature shows how necessary it is to specify the exact reaction which is taking place when discussing oxalic acid photolysis in presence of uranyl and other metallic salts. In addition to the above decomposition, the added salt can oxidise the oxalic acid, being itself reduced, or, if air be present, can act as a carrier for atmospheric oxygen. Whereas Anderson and Robinson find quantum efficiencies much below unity for the uranyl sulphate–oxalic acid mixtures, Boll (*Ann. Physique*, 1914, **2**, 256), working with 0·001*M*-solutions freely exposed to air, obtained a value for γ of 50 for light of nearly the same frequency. In this latter case, the uranyl salt was probably simply acting as an oxygen carrier. The same remark applies, perhaps in a lesser degree, to the photolysis of oxalic acid solutions in absence of a catalyst. For example, in Kailan's work (*Monatsh.*, 1913, **34**, 1209), which, for this reason, we did not quote at the beginning of this paper, the reaction being followed was again probably essentially $H_2C_2O_4 + \tfrac{1}{2}O_2 \longrightarrow H_2O + 2CO_2$.

Effect of Concentration.

The reaction being apparently unimolecular, we should expect the quantum efficiency to be independent of concentration. We tested this point by experiments with 0·01*M*- and 0·001*M*-solutions, and obtained rather unexpected results.

Experiment 10. A 0·01*M*-oxalic acid solution was exposed to the total light of lamp 2 (1·4 cm. diaphragm aperture) for 15½ hours. The yield of carbon dioxide was 116 divisions at 15°, or 110 divisions at *N.T.P.* This is equivalent to $1·65 \times 10^{18}$ molecules. The absorption of the 334 μμ and 365 μμ lines by this dilute solution was negligible. For the other groups of lines, we have calculated as follows :

λ (in μμ).	Ergs absorbed.	Quanta absorbed.	Calc. decomp. (molecules).
280—313	$5·18 \times 10^8$	$0·78 \times 10^{20}$	$0·32 \times 10^{18}$
254—275	7·68	1·02	1·02

The observed decomposition thus exceeds the calculated value of $1·34 \times 10^{18}$ molecules by nearly one-quarter.

Experiment 11. A 0·001*M*-solution was similarly insolated for 19½ hours. The carbon dioxide yield was 79 divisions, or 75 divisions at *N.T.P.* Calculating as before, and making allowance for the 8% decrease in concentration occurring during the insolation, the volume of carbon dioxide at *N.T.P* expected would be only 40 divisions, or little more than half of what was actually obtained.

It must be remembered that the quantum efficiencies used for obtaining the calculated values are average values for fairly wide spectral regions, and can only be applied for the purposes of exact calculations to cases in which the distribution of absorbed energy over the different wave-lengths comprised within the regions concerned is identical with that which held good during the experiment from which the quantum efficiency was deduced. By plotting our figures for γ against ν and against λ, and by considering the aforesaid energy distributions, we were able to arrive at a rough estimate as to the extent to which our results are affected by this factor. For Expt. 10 we found that the absorbed energy distribution in the 265 μμ group was practically identical with that in Expt. 8, but that the centre of gravity in the 300 μμ group lay roughly at about 284 μμ. The effect would be to increase the expected transformation by about 12%, and thus to halve the apparent discrepancy. In Expt. 11, the average effective absorbed wave-lengths for both spectral regions lie further in the ultra-violet than the conventional figures of 300 and 265 μμ. In the latter case, however, the shift is very small, and the total effect is only to increase the calculated decomposition by about 10%, the actually observed decomposition still being 70% more than the calculated figure.

We have done no further experiments, and therefore do not wish to lay too much stress on these results. Those of Expt. 11 are, however, certainly far outside our ordinary experimental errors. If they be accepted, it would seem necessary to assume that those oxalic acid molecules which, by absorption of a quantum, are raised to so high an energy level that they can decompose, do not do so instantaneously, but have an appreciable life in the activated condition, during which they are liable to be deactivated by collision with other oxalic acid molecules. An increase in dilution lessens the chance of such deactivation, and hence raises the quantum efficiency. It may be mentioned that, very recently, Ghosh and Mukherjee (*J. Indian Chem. Soc.*, 1925, **2**, 173) have been led to a similar conclusion in the case of activated bromine molecules undergoing reaction with tartaric acid.

Summary.

(1) The initial stages in the photolysis of aqueous oxalic acid solutions have been quantitatively investigated by specially developed experimental methods.

(2) For wave-lengths between 254 and 365 μμ, the primary reaction is $H_2C_2O_4 \longrightarrow H{\cdot}CO_2H + CO_2$.

(3) Neither hydrogen nor carbon monoxide is produced.

(4) Formaldehyde (the vapour of which is liable to be analysed as a mixture of carbon monoxide and hydrogen) is formed in small quantity, in all probability by interaction between nascent carbon dioxide molecules and water.

(5) The proportion of formaldehyde produced increases with the frequency of the light used.

(6) For solutions of concentration 0·6—0·7*M*, the number of quanta required for decomposition of 1 molecule of oxalic acid are as follows: 265 μμ, 100; 300 μμ, 245; 365 μμ, 1060.

(7) For solutions of concentration 0·01*M* and (particularly) 0·001*M*, there is evidence that the quantum efficiencies are greater than those quoted.

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UNIVERSITY OF LONDON,
KING'S COLLEGE.

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