CCCLXXX.—*The Photochemical Decomposition of Aqueous Formic Acid Solutions.*

By ARTHUR JOHN ALLMAND and LEWIS REEVE.

A FEW isolated observations have previously been recorded on the subject of formic acid photolysis. Thiele (*Ber.*, 1907, **40**, 4914; *Z. angew. Chem.*, 1909, **22**, 2472) reports that the anhydrous acid is decomposed by the light from a quartz–mercury lamp. A small quantity of a yellow, hygroscopic, and strongly acid solid is produced, whilst the gaseous products consist chiefly of carbon dioxide, but also contain oxygen, carbon monoxide, and other combustible gases. Berthelot and Gaudechon (*Compt. rend.*, 1910, **151**, 478) give the composition of the gases produced as : CO_2, 59; CO, 21; H_2, 19; CH_4, 1%. The same authors, whilst ascribing an important part in the photolysis of aqueous oxalic acid to secondary photo-decomposition of primarily-produced formic acid, bring forward no experimental work with aqueous formic acid solutions in support of their views. Indeed, the only published work on this subject is that of Kailan (*Z. physikal. Chem.*, 1920, **95**, 215), who merely records (i) that such solutions are decomposed by ultraviolet light when contained in quartz, but not in glass, vessels; (ii) that the dissociation constant of the acid is unchanged after partial photolysis and that, therefore, oxalic acid is not a product; (iii) that the velocity increases with increase of concentration, but less rapidly. Ramsperger and Porter (*J. Amer. Chem. Soc.*, 1926, **48**, 1267) report that formic acid vapour gives, on photo-decomposition, a gaseous mixture containing CO_2, 18; H_2, 18; CO, 32; H_2O, 32%.

EXPERIMENTAL.

Our own experiments, made in order to test Berthelot's suggested mechanism for photo-decomposition of oxalic acid solutions, have not been carried as far as we could have wished, but nevertheless present points of interest. The apparatus used comprised the essential features of Apparatus 4 (preceding paper), but, in addition, included, between the insolation cell and the pump, a trap containing solid potash, its purpose being to retain formic acid given off during the preliminary evacuation. Vacuum taps, suitably placed, made it possible to connect the cell with the Toepler pump (*a*) directly, (*b*) *via* the phosphorus pentoxide tube, and (*c*) *via* the potash trap and the phosphorus pentoxide tube. The preliminary evacuation could be carried out (as described in the preceding paper) efficiently and sufficiently rapidly with the above arrangement. In order to deal with the products of photolysis, a large expansion bulb was attached to the apparatus between the cell and the absorption tubes, separated from both of them by taps and leading, in its turn, by means of a vacuum tap and ground joint, to a bulb which could be cooled either in liquid air or in a solid carbonic acid–ether mixture.

The procedure adopted after insolation was (i) to evacuate the whole of the apparatus except the cell; (ii) to cool the freezing-out bulb by liquid air; (iii) all other taps being closed, to put the cell into connexion with the expansion bulb for a definite short period; (iv) to shut off the cell from the expansion bulb and connect the latter with the freezing-out bulb; (v) after sufficient time had elapsed, to pump off through the phosphorus pentoxide tube, measure, and analyse any gases which had escaped condensation at liquid-air temperature [fraction (*a*)]; (vi) to replace the liquid air in the Dewar vessel surrounding the freezing-out tube by solid carbon dioxide and ether, and then pump off, measure, and analyse as before [fraction (*b*)]. The residual contents of the freezing tube after (vi) were merely formic acid and water.

Experiment 1. After showing that the preliminary evacuation had no appreciable effect on the concentration of the formic acid solution in the cell, a $2{\cdot}40M$-solution was insolated for 18·28 hours in the total light of the quartz–mercury lamp, and the products were separated as described. Fraction (*a*), *i.e.*, gas not condensed by liquid air, measured 0·356 c.c. A portion of it gave a strong positive formaldehyde reaction with the Buchanan–Schryver test. This was surprising, as one would have imagined all formaldehyde to be condensed at liquid air temperature, recent measurements of Mali and Ghosh (*J. Indian Chem. Soc.*, 1924, **1**, 37) pointing to the vapour pressure of Kekulé's liquid formaldehyde as being of the order of 10^{-7} mm. under those conditions. It seems possible that the vapour given off from Kekulé's product does not consist of simple formaldehyde molecules, but of something more complex (no vapour density measurements appear to have been done), and that, on the other hand, unimolecular formaldehyde might be expected to behave like a permanent gas in respect of its condensation temperature. In our experiments, it is formed at room temperature and pumped off at a pressure of about 0·0005 atm. In these circumstances, its tendency to polymerise (so marked at higher temperatures and pressures) would be very much reduced.

When another portion of fraction (*a*) was subjected to sparking in the micro-gas analysis apparatus previously described, it increased considerably in volume, and subsequent analysis showed carbon dioxide to be absent and the sparked gas to consist of carbon monoxide and hydrogen, with a small residue (air from leakage). The actual results were as follows :

(*a*) Volume of gas taken	62	divisions.
(*b*) „ „ after sparking	90	„
(*c*) „ „ „ treatment with KOH	91	„
(*d*) „ „ „ addition of oxygen	173	„
(*e*) „ „ „ combustion	90	„
(*f*) „ „ „ treatment with KOH	41	„

Hence

(*g*) CO in sparked gas		49	„
(*h*) H_2 „ „		39	„
(*k*) H·CHO in original gas		28	„
(*l*) Composition of original gas	H·CHO	28	„
	CO	21	„
	H_2	11	„
	Residue	2	„

Fraction (*b*)—condensed by liquid air, but not by solid carbon dioxide and ether—had a total volume of 15·91 c.c. On treatment of a micro-portion with solid potash, it proved to be almost entirely carbon dioxide. The whole sample of 15·9 c.c. was then treated with potash in the same way. The total residue amounted to 158 divisions, or 0·0869 c.c. only. We are unable to say exactly what was the composition of this gas. It was not formaldehyde, nor did it give the latter even on long standing with water (Buchanan–Schryver test). On continued sparking, however, in absence of oxygen, its volume increased until it was about eight times that of the original sample—thus a volume originally 21·5 divisions became successively 56, 84, 144, 161, 164·5, 171·5, 172, 171 divisions, and this final figure remained unaltered even after more than 50 sparkings. The sparked gas was then divided into three portions, each of which was analysed for carbon monoxide and hydrogen. The results were :

(i) CO, 42 ; H_2, 57%. (ii) CO, 40 ; H_2, 58%. (iii) CO, 43 ; H_2, 56%.

The gas unaccounted for never amounted to more than one division (0·00055 c.c.) in any single analysis. If the total gas unaccounted for (about 2·5 divs.) be regarded as due to air leak, and subtracted from the 21·5 divs. of the original gas, then the increase in volume on sparking is nearer nine-fold than eight-fold. From this increase in volume and from the relative proportions of hydrogen and carbon monoxide contained in the sparked gases, the unknown mother-substance (x) might be imagined to have been a reduction product of some polymer of formaldehyde, of empirical formula perhaps $H_{10}(CO)_4$, formed by the action of hydrogen of great reducing power which, as we shall see, is probably produced during the photolysis. The fact that it was not frozen out at the temperature of solid carbon dioxide is, however, as remarkable as the inability of liquid air to hold the formaldehyde vapour. It has indeed been suggested to us that the expansion on sparking was merely due to gases driven out of the electrodes. Against this view, in itself not improbable, we would say (*a*) that no appreciable increase in volume was observed when sparking oxygen or nitrogen alone, (*b*) that the increase in volume caused by *one* spark (21·5 divs. becoming 56) was of quite a different order from the expansions observed when, for example, sparking gas containing formaldehyde, and (*c*) that it would be a coincidence if *both* the gases from the electrodes *and* the original gas taken were found, after sparking, to consist simply of hydrogen and carbon monoxide.

The following table contains a summary of the results of this experiment, as far as the gaseous products of reaction are concerned. Volumes are in c.c.

		Vol. formed during expt.	Vol. per hour.	Percentage of total gases.
Fraction (*a*)	H·CHO	0·161	0·0088	0·99
	CO	0·121	0·0066	0·74
	H_2	0·063	0·0035	0·39
	Total	0·345*	0·019	2·12
Fraction (*b*)	CO_2	15·823	0·8656	97·34
	x	0·087†	0·0048	0·54
	Total	15·910	0·870	97·88
Total gases		16·25	0·889	100

* Residual gases not included. † Possible residual gases included.

The formic acid solution after the experiment still contained formaldehyde (or perhaps some less volatile polymer) in comparatively large amounts. On evaporation, whether on the water-bath or in a desiccator over calcium chloride and soda-lime, no trace of solid residue could be found. On the other hand, after evaporation in the desiccator, a distinct ethereal smell was noted. This may possibly have been methyl formate or methyl alcohol, but was not characterised more closely.

Experiment 2. Another portion of 2·40M-formic acid was insolated as in the first experiment, but for 3 hours only. The yields, in c.c. per hour, of gaseous products were :

H·CHO, 0·0091 ; CO, 0·0050 ; H_2, 0·0040 ; CO_2, 0·916 ;
x, not determined exactly, but of the order of 1% of the CO_2.

The general nature of the results is as in Expt. 1, and there is fair quantitative agreement—perhaps as good as could be expected in view of the complex secondary reactions which obviously take place. As before, formaldehyde was detected in the photolyte after the insolation.

Berthelot and Gaudechon assume that frequency has a very marked effect on the products of this photolysis, the reaction $H \cdot CO_2H \longrightarrow H_2O + CO$ occurring in the wave-length region 250—300 μμ, and the reaction $H \cdot CO_2H \longrightarrow H_2 + CO_2$ being caused solely by wave-lengths shorter than 250 μμ. We accordingly directed our attention to this matter, using the filter solutions already described (preceding paper).

Experiment 3. A 2·40*M*-solution of formic acid was insolated for 16 hours by quartz–mercury lamp light which had been filtered by passage through 5 mm. of 0·075% Diamond Fuchsin solution, and therefore (apart from red light) was almost monochromatic 365 μμ radiation. No perceptible decomposition occurred, although the extinction coefficient of formic acid for this wave-length is about twice that of oxalic acid, which does undergo slight decomposition.

Experiment 4. The same solution was exposed for 13·64 hours to quartz–mercury lamp light which had passed through a filter of 5 mm. of 0·025% Auramin O (twice as concentrated as was used in the corresponding oxalic acid experiment), the transmission of which was calculated to be :

μμ	313	303	297	290	280
Transmission (%)	6·9	13·5	16·0	13·2	6·3

The gaseous products were fractionated and treated as before. Fraction *a* measured 21 divisions, was 2·8% of the total gases, and appeared to be similar in composition to the previous fractions obtained in the same way. A more definite statement cannot be made, as, on sparking before adding oxygen, the gas only expanded slightly, though definitely, in volume, and was afterwards found to contain carbon dioxide. Clearly, some air had leaked in. Fraction *b* measured 0·401 c.c. at 15°, constituted 97·2% of the total gases, and contained 97·6% of carbon dioxide. The residual 2·4% was not examined. The results of this experiment in respect of carbon dioxide evolution were thus essentially the same as those obtained in the whole light of the lamp, whereas, according to Berthelot and Gaudechon, the light used being free from short wave-length radiation, only carbon monoxide should have been produced.

Mechanism of the Reaction.

The results recorded above indicate that by far the most important product of the photolysis of a 2·4*M*-solution of formic acid, whether by the full light of the quartz–mercury lamp or by the group of lines comprised between 280—313 μμ, is carbon dioxide; that both hydrogen and carbon monoxide are formed at the same time, but only to the extent of about 0·5% of the quantity of carbon dioxide, rather more carbon monoxide than hydrogen being produced; and that considerable amounts of formaldehyde and of other reduction products of formic acid also result.

The preponderance of carbon dioxide suggests that the main reaction is $H{\cdot}CO_2H \longrightarrow CO_2 + H_2$, but it is necessary to account for the absence of the great proportion of the hydrogen demanded by this equation. We suggest that both its disappearance and the presence of formaldehyde (and probably of reduction products of the latter) can be accounted for by the assumption that the nascent or activated hydrogen molecules, in virtue of their high energy content, are capable of reducing those formic acid molecules with which they collide: $H_2' + H{\cdot}CO_2H \longrightarrow H{\cdot}CHO + H_2O$. As the formaldehyde accumulates, so it becomes available for further reduction in the same way, and the unknown complex gas x in our b-fractions, and also the substance (perhaps the same as x) noted with the ethereal smell, probably arise in this manner.

It may be remarked that, although in the case of oxalic acid photolysis we concluded that the formaldehyde was produced according to the reaction $CO_2' + H_2O \longrightarrow H{\cdot}CHO + O_2$, the same mechanism, though it may well account for some of the formaldehyde produced in the present case, cannot account for all. The quantities are greater, both absolutely and relatively; the simultaneous production of oxygen required by this equation could not have escaped notice (unless, of course, we assume the oxygen itself to be so " activated " on formation as to oxidise formic acid to carbon dioxide and water); and the deficiency in hydrogen would not be accounted for. Another possible mechanism which would account both for formaldehyde production and for hydrogen deficiency is that the primary reactions $H{\cdot}CO_2H \longrightarrow CO_2 + H_2$ and $H{\cdot}CO_2H \longrightarrow CO + H_2O$ proceed at about the same rate, and that the nascent carbon monoxide and hydrogen mutually destroy one another thus: $CO + H_2 \longrightarrow H{\cdot}CHO$. This, however, seemed unlikely. Apart from the necessity of assuming equal probabilities for the two primary decompositions, it was improbable that any but quite a small proportion of nascent carbon monoxide and hydrogen molecules would collide before deactivation had occurred.

There remained then the first suggestion of interaction between molecules of activated H_2' and of formic acid, a suggestion which could be tested very simply by varying the concentration of the formic acid, the molecules of which are assumed to act as acceptors for the H_2' molecules. An increase in its concentration should increase the formaldehyde yield at the expense of the hydrogen, whilst a decrease should have the reverse effect. We therefore carried out an insolation with a more dilute formic acid solution.

Experiment 5. A 0·113*M*-solution was insolated in the usual way by the full radiation of the mercury lamp for 7·75 hours. Owing to an accident, the gases were not completely pumped off. However, two samples were obtained, simply using solid carbon dioxide around the freezing-bulb, and thereby not separating fractions *a* and *b*, although removing water vapour and formic acid. They were measured (using a capillary tube of which one division represented 0·0119 c.c. instead of 0·000547 c.c. as hitherto) and analysed, with the following results :

Sample (i).	
CO_2	46 divisions.
CO	11 ,,
H_2	68 ,,
Total	125 ,,

Sample (ii).	
CO_2	19 divisions.
CO	2·5 ,,
H_2	15·3 ,,
Residue	2·2 ,,
Total	39 ,,

Both samples were sparked after absorption of carbon dioxide but before being analysed for carbon monoxide and hydrogen. In the first case, there was a slight increase in volume (about 7%), and in the second, no perceptible change. Formaldehyde was not detectable in the solution after photolysis.

Owing to the accident referred to, the results are not as completely conclusive as could be wished, but the following points are definitely established. (*a*) The proportion of hydrogen has been enormously increased. The quantity recovered was actually greater than the quantity of carbon dioxide, but that is, of course, due to the greater solubility of the latter—the difference between the compositions of the first and second samples is evidence of this. (*b*) This increase in the production of hydrogen is accompanied by a suppression, complete or nearly so, of formaldehyde formation. (*c*) There is a large increase in the ratio CO : CO_2 in the products of photolysis. There seems little doubt then as to the truth of our assumption—the deficiency of hydrogen and the production of formaldehyde are due to one and the same cause. The increase in the carbon monoxide content of the gases suggests, moreover, that the decrease in formic acid concentration has had a similar effect in this case as well, and that, in more concentrated solutions, the primary photolysis $H{\cdot}CO_2H \longrightarrow H_2O + CO'$ is followed by $CO' + H{\cdot}CO_2H \longrightarrow CO_2 + H{\cdot}CHO$. If that be so, the extent of the primary reaction $H{\cdot}CO_2H \longrightarrow H_2O + CO$ can in no sense be estimated from experiments with concentrated formic acid solutions. The relative amounts of hydrogen and carbon monoxide recovered during the present experiment indicate that it occurs to the extent of about one-sixth of the primary reaction $H{\cdot}CO_2H \longrightarrow H_2 + CO_2$.

If it can be assumed (as indeed most of our figures indicate) that the regular and standardised method of evacuation adopted would result in the pumping off on each occasion of a definite fraction of any dissolved gas held in purely *physical* solution, the figures quoted above would indicate that this fraction is 0·775 for the hydrogen and 0·773 for the carbon monoxide, and that there were originally present 87·7 and 14·2 divisions of these gases, respectively. The same assumption in the case of the carbon dioxide would lead to a fraction of 0·59 and a total volume of 78·4 divs. As, however, this gas is more soluble and partly present as H_2CO_3, the fraction removed on each occasion would be less, and, moreover, would fall with successive evacuations; if this be so, an original carbon dioxide volume of 87·7 instead of 78·4 divs. would not be an unreasonable figure to assume.

Energetics.

We determined the extinction coefficients of a 2·25*M*-formic acid solution by means of the spectrometer–thermopile–galvanometer method, using 5 cm. and 5 mm. layers. Our results were as follows ($\log_{10}$; g.-mol.; litre; cm.):

λ in μμ ...	365	313	303	297	290	280
k	0·003	0·006	0·0082	0·010	0·0144	0·024

λ in μμ ...	275	270	265	254	248
k	0·032	0·041	0·055	0·30	0·85

Bielecki and Henri (*Compt. rend.*, 1912, **155**, 456) give for $\lambda = 255$ μμ and 245·2 μμ, $k = 0·25$ and 2·4, respectively.

Using these data, and the results of Expts. 1, 2, and 4, we can calculate approximately, as in the preceding paper, the quantum efficiencies of this reaction for the wave-length regions 254—275 μμ (average value 260 μμ) and 280—313 μμ (average value 300 μμ). Neglecting any small possible reaction between CO_2' and water, with production of formaldehyde, the quantity of formic acid primarily decomposed is measured by the sum of the carbon monoxide and carbon dioxide formed.

Quantum Efficiency for 300 μμ.—The data used were those of Expt. 4. In 13·64 hours, the absorbed energy was

μμ	313	303	297	290	280
Ergs × 10^{-7}	1·98	1·84	0·96	0·59	0·81

the total of $6·18 \times 10^7$ ergs corresponding to $0·94 \times 10^{19}$ quanta of wave-length 300 μμ. Fraction *b* was 0·401 c.c. at 15° = 0·380 c.c. at *N.T.P.* Neglecting the small amount of carbon monoxide (a correction of the order of 0·5—1%) we have

$$\frac{0{\cdot}380 \times 0{\cdot}976 \times 6{\cdot}1 \times 10^{23}}{22400} = 1{\cdot}00 \times 10^{19}$$

as the number of molecules of formic acid decomposed. The quantum efficiency γ_{300} is therefore 1·06.

Quantum Efficiency for 260 μμ.—For this calculation, we took, from Expts. 1 and 2, 0·89 c.c. per hour as the yield of carbon dioxide produced under the standard conditions of insolation. This corresponded to a total of $22{\cdot}78 \times 10^{18}$ molecules. In the same time, $7{\cdot}29 \times 10^{18}$ quanta of light of average wave-length 300 μμ were absorbed. Using the value of $\gamma_{300} = 1{\cdot}06$ just given, this would cause the decomposition of $7{\cdot}73 \times 10^{18}$ molecules, leaving $15{\cdot}05 \times 10^{18}$ to be accounted for. The number of absorbed quanta for the 254—275 μμ spectral region was $5{\cdot}62 \times 10^{18}$ per hour (the centre of gravity being at about 260 μμ and not at 265 μμ, as was the case with oxalic acid). This gives a value for γ_{260} of 2·68.

For wave-lengths between 250 and 300 μμ, therefore, the quantum efficiencies for the primary photolysis of $2{\cdot}4M$-formic acid are about 260 times those for $0{\cdot}6M$-oxalic acid. On the other hand, they clearly fall much more rapidly for formic acid at longer wave-lengths.

Quantum Efficiency at Lower Concentrations.—It appeared of interest to check the above figures by the data of Expt. 5, taking the sum of the extrapolated volumes of hydrogen (87·7 divs.) and carbon monoxide (14·2 divs.) as a measure of the decomposition of the $0{\cdot}113M$-solution in 7·75 hours. One can calculate, as previously, that, during 1 hour, there were absorbed $11{\cdot}13 \times 10^{17}$ quanta of $\lambda = 260$ μμ and $3{\cdot}97 \times 10^{17}$ quanta of $\lambda = 300$ μμ, to which corresponds a total decomposition of $3{\cdot}40 \times 10^{18}$ molecules of formic acid. The corrected volume of carbon monoxide and hydrogen formed per hour is equivalent to $4{\cdot}00 \times 10^{18}$ molecules. If only the hydrogen be counted, the figure is $3{\cdot}45 \times 10^{18}$ molecules. We regard this improved agreement as fortuitous, and the discrepancy between the figures 3·40 and 4·00 as a real one, due to the centre of gravity of the absorbed energy in Expt. 5 lying further in the ultra-violet than in experiments with more concentrated solutions (thus, nearly 80% of the energy absorbed in the 260 μμ region was due to the 254 μμ line). The effect would be that the quantum efficiencies used for calculation would be too low, and hence also the computed yields. We consider that the extent of agreement obtained shows that, within the limits 2·40—$0{\cdot}113M$, the quantum efficiency in this reaction is independent of concentration, and we further think that it supports the view already put forward on the mechanism of the primary and secondary changes involved in the photolysis.

The evidence of collision between H_2' or CO' molecules and formic acid molecules, afforded by the production of formaldehyde and by the difference between the results of Expts. 1 and 5, suggests strongly that the same mechanism is the cause of the value of 2·68 found for γ_{260}. It would seem that the effect of such collisions will depend on the energy content of the activated molecules at the instant of collision. The higher the frequency of the light and the shorter the interval of time between the liberation of the activated molecule and its collision with a formic acid molecule the greater will be this energy content and the higher will tend to be both γ and formaldehyde yield. The value 2·68 for γ_{260} suggests the production of short reaction-chains, presumably resulting from the absorption of the larger quanta comprised in this group. The results of Expts. 1 and 5 suggest that, in the first stages of deactivation, the H_2' and CO' molecules lose the power of producing formaldehyde by collision with formic acid molecules, whilst still being able to break up the latter (*e.g.* $H_2' + H{\cdot}CO_2H \longrightarrow H_2 + H_2O + CO$). The energy content of a H_2' (or CO') molecule resulting from decomposition of formic acid by a 300 $\mu\mu$ quantum is, however, not even sufficient to cause decomposition of another formic acid molecule on collision; and this suggests that formaldehyde had not indeed been formed during Expt. 4, and that the absence of an expansion on sparking was not simply due, as we surmised, to an air leak.

Final Discussion.

Even after making full allowances for the differences between the experimental conditions of Berthelot and Gaudechon's work and our own, we find it difficult to reconcile their data and views on the oxalic and formic acid photolyses with ours. Their failure to detect decomposition of oxalic acid solutions by wave-lengths longer than 300 $\mu\mu$ is probably due to the small absorption for these wave-lengths of the thin layers of solution they used. But their statement that formic acid decomposes in two different ways above and below 250 $\mu\mu$, giving carbon monoxide plus water and hydrogen plus carbon dioxide, respectively, is directly in conflict with our own experiments. Nor can we bring into accord with our results their statement that the products of long-continued photolysis of an oxalic acid solution in the full light of the quartz–mercury lamp are solely carbon dioxide and hydrogen, without any formic acid or carbon monoxide. The production of formaldehyde during oxalic acid photo-decomposition is mentioned by them only incidentally, and is not reported as occurring during the photolysis of anhydrous formic acid, although our results with solutions make it probable that it is, at all events, an intermediate product in that case as well.

Possibly Berthelot and Gaudechon in some cases mistook formaldehyde vapour for a mixture of carbon monoxide and hydrogen, as we did at the beginning of our work. Very probably their working temperatures were rather high, as seems to have been the case in most of their photochemical work. In such circumstances, the formaldehyde would largely be given off from the oxalic acid solution as vapour, and would undergo photo-decomposition to hydrogen and carbon monoxide, together with some carbon dioxide and methane, as both they (*Compt. rend.*, 1910, **150**, 1690) and von Goldberger (Diss., Karlsruhe, 1915) found. It is significant that methane is mentioned by them as one of the products of photodecomposition of anhydrous formic acid. Possibly also under their conditions—higher intensities than we used and also probably a greater proportion of shorter wave-length light—considerable formation of the reducing sugars (noted by Baly, Heilbron, and Barker) took place, but was not tested for. In any case, with such differences in experimental conditions, a quantitative comparison of any sort between their results and ours is out of the question—thus it is quite easy to show, from our quantum efficiency, energy distribution, and absorption experiments, that any secondary decomposition of primarily-produced formic acid during our oxalic acid experiments would be quite negligible, whereas it probably did happen in some of their work. The quantitative discrepancies are nevertheless surprising.

With regard to Volmar's calculations, it is only necessary to say that our experiments do not confirm them. He gives 320 and 210—220 μμ as the threshold wave-lengths for oxalic acid and formic acid photolysis, respectively—we find decomposition at 365 and 280—313 μμ, respectively. It may be added that, according to Franck (*Z. Elektrochem.*, 1925, **31**, 350), there is no sound theoretical basis for such calculations.

Summary.

(1) Light of wave-length 250—300 μμ decomposes formic acid according to the two primary reactions, $H{\cdot}CO_2H \longrightarrow CO_2 + H_2'$ and $H{\cdot}CO_2H \longrightarrow CO' + H_2O$, the former probably taking place to the extent of about six times the latter.

(2) If the formic acid solution be sufficiently concentrated, the greater part of the nascent hydrogen and carbon monoxide molecules, more particularly the former, undergo secondary reaction with the formic acid, giving formaldehyde and still more highly reduced products.

(3) The quantum efficiencies for formic acid decomposition in 0·11—2·4*M*-solutions are of the order of 1·0 for 300 and 2·7 for 260 μμ.

(4) The work of Berthelot and Gaudechon on the photolysis of oxalic and formic acids is discussed in the light of the experimental facts here presented.

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UNIVERSITY OF LONDON,
KING'S COLLEGE.

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