76. *The Action of Light on Mixtures of Ozone and Chlorine. Part II. Results with High Ozone Concentrations. Discussion.*

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It was mentioned in Part I (J., 1931, 1652) that a mist was produced when a chlorine–ozone mixture was insolated. Owing to the position of the reaction cell in the thermostat, this phenomenon escaped notice for some time, and was first observed when the spectral absorption of such a mixture was being determined by means of a monochromator–thermopile–galvanometer combination. This mist formation was now connected with a fact previously noted, *viz.*, that the transmission for 365 μμ of a reaction mixture low in chlorine content increases during the first few minutes of insolation, then becoming constant. The natural conclusion was that some reaction was taking place whereby chlorine was being removed from the gaseous system, and that its disappearance was only detectable optically when it was in low concentration and when light of high extinction coefficient ($\alpha_{365} = 27{\cdot}17$) was used.

Accordingly, the cell then in use was cut down after all chlorine and ozone had been displaced, and examined. A thin moist film was found on the walls. This was washed out and tested. It gave a negative reaction for chloride, which became positive after boiling with ferrous sulphate and sulphuric acid, thus indicating the presence of chlorate. A simple piece of apparatus was then set up, consisting essentially of a glass bulb with entry and exit tubes, through which a chlorine–ozone mixture was allowed to stream at about 2 litres/hour. The upper part of the bulb was illuminated with 365 μμ radiation, and the lower part cooled in ice. After 7 hours, the bulb was washed through with air, and the thin film of deposited mist dissolved in a little water and examined. It gave negative tests for free chlorine, hypochlorite, chloride, and sulphate. A drop added to a drop of concentrated potassium chloride solution gave an immediate precipitate of potassium perchlorate, identified microscopically. Similarly, a drop added to a drop of 2% brucine in dilute acetic acid threw down the same characteristic clusters of six-sided plates, radiating from nuclei, as given by potassium perchlorate. Reduction by either sulphur dioxide, acidified ferrous sulphate, or titanous sulphate resulted in the formation of chloride, and its production by the first two reducing agents indicated the presence of chlorate as well as perchlorate.

The conclusions appear obvious. Chlorine trioxide (ClO_3) is formed as an intermediate stage in the photochemical reaction.

The gases used contain a certain amount of water vapour derived from the cell walls (not baked out before use), and the mist formation and increase in transmission are due to the dehydration of the mixture in accordance with the equation $2ClO_3 + H_2O \longrightarrow HClO_3 + HClO_4$, with or without the intermediate formation of chlorine hexoxide (Cl_2O_6).

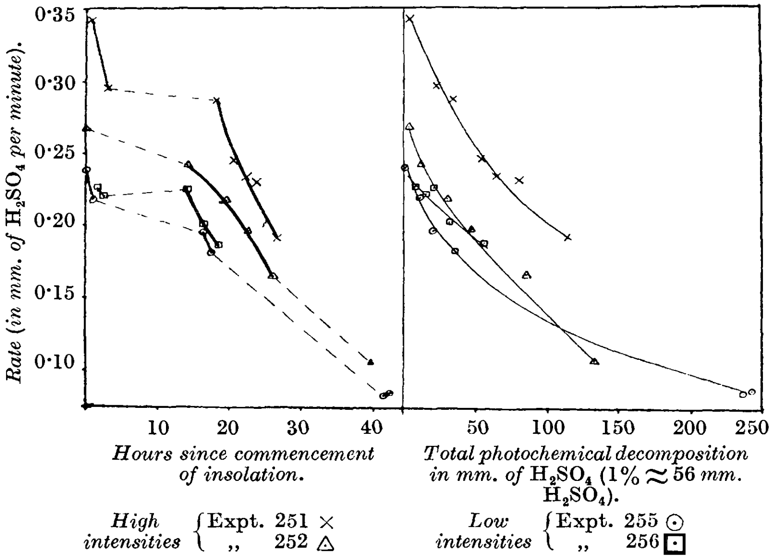
We were at that time considering our results in the light of a modification of a hypothesis put forward some years ago (Allmand, *Trans. Faraday Soc.*, 1926, **21**, 603) to account for the order of the reaction in respect of ozone. It was then suggested that the reaction mechanism involved the primary formation of activated chlorine molecules, that these, in addition to decomposing ozone directly, could activate oxygen molecules by impact, and that these activated molecules could effect the decomposition of ozone molecules by collision. On the assumption of relatively long lives for Cl_2' and O_2' molecules, it was shown that the resulting kinetic equation was of zero order for ozone. The modified theory involved the substitution of chlorine atoms and chlorine peroxide molecules for Cl_2' and O_2' molecules respectively. The discovery that the trioxide played a part in the decomposition suggested that the postulated interaction between the peroxide and ozone was simply $ClO_2 + O_3 \longrightarrow ClO_3 + O_2$. We accordingly prepared a mixture of the peroxide and carbon dioxide (Bray, *Z. physikal. Chem.*, 1906, **54**, 575) and carried forward the gases by a current of air, first over phosphoric oxide and then into a blackened bulb, into which dry ozone was also passed. After an hour, the whole was blown out with dry air, and red drops of Cl_2O_6 were found. Analysis showed the liquid not to be quite pure, but to contain some heptoxide. As, however, the paper of Schumacher and Stieger (*Z. anorg. Chem.*, 1929, **184**, 272) appeared shortly after our experiments, we did not pursue the matter further.

Although the modified theory mentioned had proved successful in one of its main predictions, it was nevertheless soon abandoned, partly because it would have involved the formation of chlorine peroxide in insolated mixtures of chlorine and oxygen, and, in spite of the very characteristic spectrum of this oxide, no trace of such formation could be detected, and partly because of work, now to be described, carried out with concentrated ozone mixtures. These experiments were suggested by certain results recorded in Part I, particularly by the fact that, with low chlorine concentrations and 365 $\mu\mu$ light, there were indications both of a chain reaction and of an $I^{0\cdot5}$ relation. The proof of the production of the trioxide was, of course, in agreement with these indications, as also were the experiments of Bodenstein, Padelt, and Schumacher (*Z. physikal. Chem.*, 1929, *B*, **5**, 209) on the thermal reaction in chlorine–ozone mixtures.

Working with concentrated ozone, they had deduced a mechanism involving the intermediate formation of chlorine trioxide (a mist yielding perchloric acid was produced in presence of moisture) and their kinetic equation, introducing $[Cl_2]^{0·5}$, clearly suggested an $I^{0·5}$ relation in the corresponding photochemical reaction.

Concentrated ozone was prepared by the method of Riesenfeld and Schwab (*Ber.*, 1922, **55**, 2088). A bulb was sealed into the apparatus between the ozoniser and the cells, sampling bulb, and pump line. It was immersed in liquid air, and ozonised oxygen admitted intermittently, the uncondensed oxygen being pumped off every 2—3 minutes between admissions. In this way, a deep violet liquid mixture of ozone and oxygen resulted, and the condensation of excess of liquid oxygen was minimised. When the required amount of liquid had been collected, the apparatus was evacuated by the water-pump, and the liquid air removed from the ozone supply. After evaporation of the ozone and equalisation of temperature, the pressure was adjusted to one atmosphere by establishing connexion with the ozoniser. The chlorine was introduced, either at the start, by incompletely evacuating the previous filling from the cells, or else at this stage, by removing a certain fraction of the ozonised oxygen and replacing it by chlorine. All the measurements were done with 5-cm. Geräte-glas cells and 365 $\mu\mu$ radiation. Table I gives a summary of the results (γ = quantum efficiency), and the course of the experiments is shown in Fig. 1,

FIG. 1.



where the rate of decomposition is plotted against (*a*) the total quantity of ozone *photochemically* decomposed up to that point and (*b*) the *total* time since the beginning of the experiment.

TABLE I.

Expt. No.	$[Cl_2]$, % (approx.).	Percentage absorption of incident light energy.	$[O_3]$, % initially.	Apparent values of γ. At start.	At finish.	Decrease in $[O_3]$ percentage due to action of light.
251	4	41·6	20—30	6·57	3·63	2
252	1·2	23·8	34	9·0	3·47	2·3
253	0·5	11·2	25	13·4	11·5	0·3
255	0·5	11·2	40—50	>24	10	4
256	0·6	12·4	68	25·3	22·8	0·5

The γ values are considerably higher than those obtained with dilute ozone fillings, and there is evidence that, in the concentration range covered, the initial figures increase with decreasing chlorine and with increasing oxygen concentration. A striking point is that these initial values appear to fall off rapidly while the ozone concentration is still very high. Thus, in Expt. 252, if thermal decomposition could be neglected, $[O_3]$ would still be 31·7% at the end of the run, whilst the γ value of 3·47 is already near the figure found (Part I) for cell fillings with about the same concentration of chlorine but $< 8\%$ of ozone.

Unfortunately, although we were aware that the thermal rates of decomposition were relatively high in these experiments, the importance of measuring them systematically was not realised at the time and this introduces an element of doubt into the interpretation of our results. Our gas mixtures were not analysed after the experiments, nor have we the data for the accurate calculation of their compositions, either during or at the end of the experiments. We cannot therefore say with certainty to what extent the remarkable fall observed in γ is merely the natural result of decreasing ozone concentration. However, the incomplete evidence strongly points to the presence of another effect. The apparent rate of photochemical action is, of course, the total reaction in the insolated vessel less the dark reaction in the unilluminated cell. The latter can be calculated, at least approximately, from the thermal measurements of Bodenstein, Padelt, and Schumacher (*loc. cit.*), who give values for the velocity constant at 50° and 35°. Their data also allow of a rough computation of the length of the induction period which elapses before the dark decomposition reaches its maximum velocity. But the true effect of the light is not equal to the apparent effect thus calculated, for the case is one in which the total reaction on insolation is not composed additively of a light and of a dark effect (Berthoud, *J. Chim. physique*, 1926, **23**, 251). Further, owing to the extra decomposition caused by light, the contribution of the thermal reaction to the total velocity in light will tend to be less than corresponds to the reaction in the dark cell.

As a result of our calculations, making extreme assumptions regarding the thermal rates of reaction and the ensuing decreases in ozone concentration, and taking into account indications furnished by differential dark reaction rates observed between insolations, we conclude (i) that for the first 12—24 hours, depending on the experiment, thermal effects of any kind are negligible; (ii) that consequently the initial values of γ recorded in Table I are to be relied on quantitatively; (iii) that the maximum rates of thermal reaction are of the same order as the apparent photochemical rates under our conditions of insolation; and (iv) that a real decrease in γ takes place during insolation of these rich ozone mixtures, quite apart from any accompanying change in concentration, whether caused thermally or photochemically. It may be added that, in respect of initial rise, final fall, and after effect, concentrated ozone mixtures presented no unusual feature.

The effect of intensity variation was studied during the above experiments by interposing a perforated metal screen in the beam, the average velocity when the screen was used being compared with the average velocity with unweakened light before and after the screen experiment, or *vice versa*. The results are shown in Table II.

TABLE II.

Expt. No.	$[O_3]$, % initially.	Ratio of intensities.	Ratio of velocities.	Square root of ratio of intensities.	Decrease in $[O_3]$ percentage due to action of light.	Apparent γ with the higher intensity.
251	20—30	2·39	2·15	1·55	0·25	6·1
		2·37	2·14	1·54	0·8	5·1
252	34	2·33	1·53	1·53	0·4	7·6
		2·33	2·03	1·53	0·7	6·9
255	40—50	2·3	1·45	1·52	0·12	24
		2·3	1·44	1·52	0·4	
		2·3	1·50	1·52	0·45	20·5
		2·3	1·52	1·52	0·65	
		2·3	1·68	1·52	4·2	9·9
256	68	2·3	1·39	1·52	0·25	25·3
		2·3	1·31	1·52	0·5	22·8

In all cases, the velocity increases less rapidly than the intensity, and to a more pronounced degree the higher the initial ozone concentration. There seems to be a tendency for the effect to become less marked as the experiment proceeds (with decrease in γ). In Expt. 256, the velocity appears to increase less rapidly even than $I^{0\cdot5}$, and we are unable to explain the discrepancy, which seems outside our experimental error. This relation between rate and I means that γ increases with decreasing I. The highest actually measured value ($\gamma = 59$) was observed during the course of Expt. 256 when using the Corning Filter G. 586 AW (Part I, p. 1656), which has a low transmission, together with the perforated screen.

When the influence of temperature was investigated, a marked effect was found, in striking contrast to the results given by more dilute ozone fillings. Three experiments were done, the chlorine concentration being low in each case, and the initial ozone concentration ranging up to 66%. Owing to the rapid rate of change of γ, it was not easy to obtain comparable velocities at two different temperatures (30° and *ca.* 23° were used), and our figures for the three experiments were (for 10°) 1·94, 1·39, and 1·52. Of these results, the third corresponds to the most satisfactory experiment.

Discussion.

Any complete theory of this reaction must account for the following two sets of facts, separated provisionally for reasons which will appear later.

(*a*) Zero order for ozone with fairly high chlorine concentration and ozone concentration up to 7%; γ values of 2—3; proportionality between rate and I.
(*b*) For 365 μμ, $[O_3] < 7\%$, and $[Cl_2] < 2$—3%, increase in γ and departure from I_0 relation.
(*c*) An accentuation of the tendencies under (*b*) when the ozone concentration becomes high.
(*d*) $\gamma_{313} > \gamma_{365} > \gamma_{420} > \gamma_{436}$ for a given dilute ozone mixture.
(*e*) Temperature coefficient of 1·0 for a dilute ozone mixture.
(*f*) Temperature coefficient of 1·5 (*ca.*) for a rich ozone mixture.
(*g*) Detection of ClO_3 (Cl_2O_6) in the reacting gases.
(*h*) The initial rise and the final fall.
(*i*) The induction period and the after effect.

(*j*) The final rise.
(*k*) Occasional irregular and irreproducible results during induction period and after effect.
(*l*) Unusual behaviour of mixtures insolated in quartz cell.
(*m*) Rapid decrease of γ with time observed with high ozone concentration.

Of these facts, (*h*) and (*j*) were observed by Weigert (*Z. Elektrochem.*, 1908, **14**, 591), and (*a*) by Weigert and later by Bonhoeffer (*Z. Physik*, 1923, **13**, 94), and the essential criterion of former theories of the reaction was whether or not they could explain satisfactorily this last result. Such theories, all involving the primary formation in light of activated chlorine molecules and coupled with special postulates regarding their length of life or their power of isochromatic fluorescence, were put forward by Weigert (*Z. physikal. Chem.*, 1923, **106**, 407), by Bonhoeffer (*loc. cit.*) and by Allmand (*loc. cit.*), and led to formal explanations of the fact in question. They can no longer be upheld, for, in accordance with Franck (*Trans. Faraday Soc.*, 1926, **21**, 536), it is now generally admitted that the absorption of a quantum of blue or ultra-violet light by a chlorine molecule causes the immediate dissociation of the latter, and hence chlorine atoms must be regarded as the primary photocatalyst in the present case.

Two alternative mechanisms on this basis have indeed been proposed by Cathala (*J. Chim. physique*, 1928, **25**, 182), but they are untenable for a variety of reasons, including one cogently put by Griffith and McKeown (" Photoprocesses, etc.," 1929, p. 603). More recently, Schumacher and Wagner (*Z. physikal. Chem.*, 1929, *B*, **5**, 199) have suggested $Cl_2 + h\nu \longrightarrow 2Cl$; $Cl + O_3 \longrightarrow ClO + O_2$; $2ClO \longrightarrow Cl_2 + O_2$. This gives a quantum efficiency of 2, and ClO groups have been successfully used in explaining the mechanism of the chlorine-sensitised union of carbon monoxide and oxygen (Bodenstein, Lenher, and Wagner, *ibid.*, 1929, *B*, **3**, 459). Apart, however, from not accounting for certain experimental facts established by us, the above scheme involves the improbable assumption that reaction between ClO and O_3 must have a very high activation energy. Further, we cannot admit that, with excess of ozone present, the absence of a chlorine peroxide spectrum is a reason for denying the intermediate formation of this substance.

Of the facts just referred to, the most important is the demonstration that ClO_3 radicals are very probably formed during the reaction. This naturally suggests $Cl_2 + h\nu \longrightarrow 2Cl$; $Cl + O_3 \longrightarrow ClO_3$; $2ClO_3 \longrightarrow Cl_2 + 3O_2$. The quantum efficiency would again be 2, and it is of interest that this mechanism was proposed years back by Bodenstein (*Z. Elektrochem.*, 1913, **19**, 840). But in addition, there is the fact of chain formation to consider [(*b*) and (*c*)]. The most obvious conclusion is that ClO_3 is the catalyst which continues the chain, its disappearance in accordance with the above equation accounting for the $I^{0.5}$ relation. Two chain mechanisms appear possible :

(I.)	(II.)
(i) $ClO_3 + O_3 \longrightarrow ClO_2 + 2O_2$	(i) $ClO_3 + O_3 \longrightarrow Cl + 3O_2$
(ii) $ClO_2 + O_3 \longrightarrow ClO_3 + O_2$	(ii) $Cl + O_3 \longrightarrow ClO_3$.

Of these, I (ii) has been shown to take place readily, whilst I (i) is a new reaction. Mechanism II also introduces one new reaction only, for II (ii) is already assumed to take place in any case. It seems difficult to choose between the probabilities of I (i) and II (i); the former is rather the more exothermic of the two, but their activation energies would probably be similar.

The above simple scheme, whichever of the alternative chains be used, accounts satisfactorily for practically all of the first group of experimental facts (*a*)—(*i*), but fails to explain the second group, *viz.*, (*j*)—(*m*). Of these, (*k*), (*l*), and (*m*) have been sufficiently described (Part I), but further details are given about the final rise phenomenon. Normally, this set in when the ozone concentration had fallen to 0·1%. At this point, the p–t curve began to steepen, and just before the sudden change in direction at complete decomposition, its slope was usually 2—3 times as steep as in the constant slope region (Part I, Fig. 3, *a*—*d*). It was clearly shown (*e.g.*, Part I, Fig. 3, g_1, g_2) that the phenomenon is purely photochemical, and is accompanied by no abnormal after-effect. The difference between the final pressure when decomposition was complete, and the value the pressure would have had at the same instant if the constant rate of decomposition had continued, was about 2 mm. of sulphuric acid, apparently independent of the size of cell (5 or 10 cm. depth), of λ, and of chlorine concentration. If allowance be made for the fact that, in the one case but not in the other, the heat of reaction is exerting an effect on the pressure (see later), then this pressure difference would be about 2·5—3 mm. of sulphuric acid.

These unexplained facts have one feature in common, *i.e.*, they all suggest some effect of surface. Thus the final rise is very similar to the last stage in the thermal bromine–ozone reaction, shown by Lewis and Schumacher (*Z. physikal. Chem.*, 1930, *B*, **6**, 423) to be due to the sudden release of large amounts of gas from the surface of the reaction vessel. The abnormal pressure changes sometimes observed point in the same direction. Unless the very unlikely assumption is made that some gaseous inhibitor is produced during the photolysis of the rich ozone mixtures, it seems impossible to explain the fall in γ by means of a homogeneous gaseous reaction. To this evidence we may add that Cl_2O_6 formation from ClO_3 is said by Bodenstein and Schumacher (*ibid.*, 1929, *B*, **5**, 233) to be apparently assisted by surface action. As a result of such considerations, we are led to propose the following general scheme for the reaction.

(1) $Cl_2 + h\nu \longrightarrow 2Cl$
(2) $Cl + O_3 + M \longrightarrow ClO_3^* + M$
(3) $ClO_3^* \longrightarrow ClO_3$
(4) $ClO_3 \longrightarrow \mathbf{ClO_3}$
(5) $2\mathbf{ClO_3} \longrightarrow Cl_2 + 3O_2$
(6) $2\mathbf{ClO_3} \longrightarrow \mathbf{Cl_2O_6}$
(7) $\mathbf{Cl_2O_6} \longrightarrow Cl_2 + 3O_2$

(A.)	(B.)
(8) $ClO_3^* + O_3 \longrightarrow ClO_2 + 2O_2$	(10) $\mathbf{ClO_3} + O_3 \longrightarrow ClO_2 + 2O_2$
(9) $ClO_2 + O_3 \longrightarrow ClO_3 + O_2$	(9) $ClO_2 + O_3 \longrightarrow ClO_3 + O_2$

Substances in heavy type are supposed to be adsorbed on the surface of the cell. Equations (1)—(7) represent the reaction when there is no chain formation; (A) and (B) represent two distinct chain mechanisms, to which very different characteristics are ascribed. The reaction $ClO_3 + O_3 \longrightarrow Cl + 3O_2$, whether in the gas or on the surface, is no longer considered. It gives final equations identical in form with those furnished by the proposed mechanism, but is less simple from the present point of view, and presents no compensating advantages.

In detail, our suggestions are as follows. According to Bodenstein, Padelt, and Schumacher (*loc. cit.*), the homogeneous gas reactions $ClO_3 + O_3 \longrightarrow ClO_2 + 2O_2$ and $2ClO_3 \longrightarrow Cl_2 + 3O_2$ require activation energies of 11·85 and 11·48 Cals. respectively, and consequently take place with difficulty at room temperature. We imagine the latter reaction practically never thus to take place, and the former (8) only to do so when the ClO_3 group concerned is freshly formed by (2), and carries with it a *sufficient surplus of energy* derived, *via* the chlorine atom, from the absorbed quantum concerned in (1). Such freshly formed groups are denoted by ClO_3*. Any such surplus energy will, of course, be dissipated during (8), and ClO_3 groups formed by (9) are not capable of continuing chain (A), which is therefore limited to a maximum of one term.

This being the case, such ClO_3 groups [from (3) and (9)] will ultimately be adsorbed on the vessel walls [(4)]. We imagine that impact of an ozone molecule on such an isolated adsorbed ClO_3 group will, subject to an energy of activation, lead to reaction (10), and will be succeeded by desorption of ClO_2, followed by (9). In addition to reaction with ozone, the reaction of ClO_3 groups with one another is also supposed to be facilitated by their adsorption and, relatively to (10), to a greater extent as the available surface becomes covered with sorbate. We imagine that their decomposition to chlorine and oxygen may proceed either directly [(5)], or with preliminary formation of Cl_2O_6 [(6) and (7)]. Finally, we suppose the adsorbing and activating properties of the various glass and quartz surfaces used to have varied considerably, not merely from one vessel to another, but also from one part to another of the same cell.

On the above basis, assuming small relative absorption of light and the setting up of a stationary state in the whole heterogeneous system, the following general expressions will hold for reaction velocity and for γ.

$$-\frac{d[O_3]}{dt} = 2k_1I_0[Cl_2] + 2k_1I_0[Cl_2]\frac{2k_8[O_3]}{k_3 + k_8[O_3]} + 2k_{10}[O_3]\left(\frac{2k_1I_0[Cl_2]}{k_5 + k_6}\right)^{0\cdot5}$$

$$\gamma = 2 + 4\frac{k_8[O_3]}{k_3 + k_8[O_3]} + 2k_{10}[O_3]\left(\frac{2}{(k_5 + k_6)k_1I_0[Cl_2]}\right)^{0\cdot5}$$

If equations (1)—(7) only are concerned, then each of these two expressions contains on its right-hand side the first term only. The second term enters if (8) and (9) are operative, and the third term if (10) plays a part. In this case, it will be noticed that two other velocity constants for reactions taking place in the surface film appear, *viz.*, k_5 and k_6, in addition to k_{10}. Inspection of the reaction scheme will also show that the liberation of oxygen in accordance with the first, second, and third terms of these equations takes place respectively on the vessel walls, in the gas space, and both on walls (two-thirds) and in gas space (one-third).

An examination of the summary of experimental facts given earlier shows that they are adequately explained by the above reaction scheme. Equations (2)—(4) account for the appearance of mist in imperfectly dried gases, for their increase in transmission, and for the formation of chloric and perchloric acids. The initial rise and final fall are explicable by the slight warming of the gases during insolation, owing to (i) the absorption of light energy (Budde effect) and (ii) the heat of reaction (Draper effect). If the insolation be interrupted whilst ozone is still present in the gases, initial rise and final fall are consequently identical, or practically so. If, however, it be continued until all ozone is decomposed the final fall is less than the initial rise, owing to the absence of any reverse Draper effect. In our experiments, these Budde and Draper effects were of the same magnitude, the former being rather greater in experiments where γ was low, and the latter being greater in experiments with high ozone concentration. If a mixture of chlorine and oxygen were insolated, the Budde effect only was obtained, corresponding to the final fall after complete decomposition.

The magnitudes of these different pressure changes are not in complete agreement with the view put forward—thus, the reaction heat component of the pressure rise is relatively a little smaller than that calculated from the known heat of reaction, the size of the quantum, and the measured quantum efficiency. The probable cause of this difference is that, in accordance with equations (5)—(7), the reaction heat is liberated in the surface layers on the cell walls which are in direct contact with the thermostat water, whereas the Budde effect component is set free in the interior of the gas.

The induction period is due to the fact that, until the stationary state is set up, reactions (1)—(4), which result in a pressure decrease, are more important than reactions (5)—(10), which bring about either the formation of chlorine and oxygen from the adsorbed layer or the transformation $2O_3 \longrightarrow 3O_2$. The after-effect is the result of (4)—(7) and (9)—(10), and will cease when all ClO_3 in the gas phase and all immediately available ClO_3 on the walls have disappeared. We say *immediately* available, as we imagine that, when the after-effect ceases, there is still ClO_3 on the cell walls in a relatively stable state, either adsorbed in such a way as to make it less rather than more reactive, or else present as Cl_2O_6. And we suppose that the final rise, which has been shown to be a photochemical effect, is caused by chlorine atoms formed in the gas, no longer finding any ozone molecules with which to combine, arriving at the cell walls, and catalysing the decomposition of the deposit on them.

The specific and local effects of surface are responsible for the unusually long induction period sometimes observed with freshly cleaned cells, and in particular, for the curious behaviour of quartz cells. Thus, the abnormal induction and after-effects noted in that case signify that k_5 and k_6 were relatively low on the quartz surface, with a consequent large accumulation of adsorbed ClO_3 during the early stages of the insolation. In addition, the apparent values of γ were low, and there was a tendency towards a reaction of the $I^{0{\cdot}5}$ type under unusual conditions of concentration and intensity. Low values of k_5 and k_6, and a continued accumulation of ClO_3 on the cell walls explain these facts also.

With regard to the general equations for the complete reactions, it is plain that, when $[O_3]$ is very low, the first term will be all important, that if $k_8[O_3]/k_3$ is sufficiently high, the second term will become significant as $[O_3]$ increases, but that at still higher values of $[O_3]$, k_{10} being now assumed to be large enough compared with k_5 and k_6, the third term will tend to be the most important of the three. Further, as long as only the first two terms are operative, the velocity will be proportional to I_0, but, as the third term becomes prominent, so there will be a tendency towards the $I^{0{\cdot}5}$ relation. Expressed differently, a high rate of light absorption will favour the first two terms of the equations.

The majority of the facts observed with dilute ozone mixtures [(*a*), (*d*), (*e*)] are accounted for by these first two terms. The second is capable of contributing a maximum of 4 to the observed γ values. Its actual contribution varies between 0 and 1, and is determined by the value $k_8[O_3]/k_3$, or, at constant $[O_3]$, by k_8. In accordance with considerations already discussed, k_8 will increase with increasing frequency, whence the effect of λ on γ actually observed. Any influence of $[O_3]$ on γ in this region will clearly be small, and was not noticed by us. The same applies to any possible, but unlikely, effect of temperature.

If the rate of light absorption falls below certain limits, then, under otherwise unchanged conditions, the third term increases in importance, γ will rise, and the rate will no longer be proportional to the intensity. This agrees with (*b*). The same happens if $[O_3]$ be raised above certain limits [(*c*)]. At the same time, the temperature coefficient, insignificant when $[O_3]$ is low, now becomes important [(*f*)]. This effect clearly is concerned with the chain mechanism, and is in agreement with the conclusion that (10) requires a moderate energy of activation. Finally, there is the fact of the very rapid decrease of γ with time when concentrated ozone mixtures are used, accompanied by a tendency towards a reversion to an I_0 type of reaction, but by no abnormal immediate after-effect. This is expressed formally by saying that $k_{10}/(k_5 + k_6)^{0 \cdot 5}$ must rapidly decrease as the reaction proceeds, and we suggest that it is essentially k_{10} which is affected. We have assumed that isolated adsorbed ClO_3 groups are those which react with ozone in accordance with (10). At the beginning of insolation, all such groups will be isolated and consequently reactive. As the available surface fills up, such groups will fall within one another's sphere of influence, and may indeed unite to form Cl_2O_6; and we assume that impacts of ozone molecules on Cl_2O_6 molecules are unfruitful, or at least do not go further than the stage of $Cl_2O_7 + O_2$, with no subsequent chain. An alternative is the assumption that only certain favoured spots on the cell walls can, by adsorption of ClO_3 groups, activate them for reaction with ozone. At the commencement of insolation, these regions are freely available, but as the reaction proceeds, and the surface concentration of ClO_3 (and Cl_2O_6) increases, the majority of the new ClO_3 groups formed by (2) are adsorbed at points where further reaction with ozone is excluded.*

One matter remains for elucidation, *viz.*, the magnitude of the effects ascribed to the adsorbed layer on the vessel walls. Considering a 10-cm. cell, we have the following approximate data:

Volume of cell, 190 c.c.
Contents at 25° and 1 atmos., $4 \cdot 7 \times 10^{21}$ molecules.
Molecules corresponding to 1% by vol., $4 \cdot 7 \times 10^{19}$.
Molecules corresponding to 1 mm. pressure of H_2SO_4, $8 \cdot 2 \times 10^{17}$.
Area of cell walls (sides only), 160 cm.^{2}.
,, ,, ,, (sides and ends), 200 cm.^{2}.
Number of molecules corresponding to a unimolecular layer on walls:
(*a*) Molecular diameter 4×10^{-8} cm., 1—$1 \cdot 25 \times 10^{17}$.
(*b*) Molecular diameter 2×10^{-8} cm., 4—5×10^{17}.

The walls being assumed to be covered with Cl_2O_6 molecules of 4×10^{-8} cm. diameter, formed from the gas phase in accordance with $Cl_2 + 2O_3 \longrightarrow Cl_2O_6$, the corresponding drop in pressure would

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* Possibly (10) necessitates prior adsorption of ozone molecules.

be 0·45 mm. of sulphuric acid. The decomposition of such a unimolecular layer in accordance with $Cl_2O_6 \longrightarrow Cl_2 + 3O_2$ would cause a pressure rise of 0·6 mm. of sulphuric acid.

The after-effects observed varied considerably, but in glass were about 0·5—1 mm. The effect of the induction period on the position of the constant slope portion of the *p–t* curve was of the same order. In quartz these figures were far greater (Part I, Fig. 4), and some of the pressure changes would correspond to layers perhaps 30 molecules thick on the cell walls. The quantity of chlorine required even for this amount of deposit would, however, only amount to 0·07% by volume. In the case of the final rise, the maximum measured rate of pressure increase was perhaps 2·5—3 times the rate during the previous " constant slope." Moreover, the net pressure increase, allowing for the disappearance of the reaction heat, has been seen to be about 2·5 mm. of H_2SO_4. This corresponds to an increase of about 20×10^{17} molecules in the gas space, or, assuming them to be formed in accordance with the equation $Cl_2O_6 \longrightarrow Cl_2 + 3O_2$, to the decomposition of 5×10^{17} molecules of Cl_2O_6. This represents a quadrimolecular layer if the molecular diameter, as before, is taken as 4×10^{-8} cm. And the observed rate of development of this extra pressure can be plausibly explained on the assumption that impact of a chlorine atom on an adsorbed Cl_2O_6 molecule brings about the decomposition of the latter. If, of course, to these molecules be attributed a diameter of 2×10^{-8} cm., then the layer photochemically decomposed during the final rise would be unimolecular.

The Thermal Reaction between Chlorine and Ozone.

It is natural to attempt to apply our results to the corresponding thermal reaction, worked out by Bodenstein, Padelt, and Schumacher (*loc. cit.*), particularly as our data with concentrated ozone mixtures make it likely that the two mechanisms must be very similar. If this is done, then it is necessary (*a*) to substitute $Cl + ClO_3$ for $ClO + ClO_2$, given by them as the primary products of interaction and, (*b*) to assume, in accordance with our equations (4)—(7) and (9)—(10), that the walls of the vessel play an essential part in the continuance and breaking of the chains. The two points are, of course, in no sense related to one another, and can be considered separately.

We have done no work on the thermal reaction, and do not feel qualified to discuss it in detail, more particularly as our own temperature-coefficient measurements with concentrated ozone, which afford in principle one of the best means of comparison, are clearly only of qualitative value. What is probably the most reliable figure, *viz.*, 1·52, gives an activation energy of 7·4 Cals., which, on our interpretation, must be equal to $q_3—\frac{1}{2}q_4$, these being the activation energies of the corresponding reactions of Bodenstein, Padelt, and Schumacher. According to these authors, $q_3—\frac{1}{2}q_4$ is 6·11 Cals. It is, of course, quite possible that, at 50°, the reactions in question take place almost exclusively in the homogeneous gas phase, whilst at 25° they take place largely in the adsorbed layer, and we have made it clear that a doubtful point in our work is the difficulty of deciding to what extent the reaction $ClO_3 + O_3 \longrightarrow ClO_2 + 2O_2$ actually does take place in the gas phase. In support, however, of the possibility that, even at 50°, the chain reaction may take place in accordance with our mechanism, we would mention one point which seems to render uncertain the deductions of Bodenstein and his colleagues. It is that, although it is twice stated elsewhere (*Z. physikal. Chem.*, 1929, *B*, **5**, 207, 234) that the reaction $2ClO_3 \longrightarrow Cl_2 + 3O_2$ will play a very minor part at room temperature, Cl_2O_6 being formed instead, nevertheless their quantitative treatment of the reaction mechanism essentially rests on the assumption (*loc. cit.*, p. 224) that, at 15°, chlorine and oxygen are the sole products of reaction.

Summary of Parts I and II.

(1) The photodecomposition of ozone, sensitised by chlorine, has been studied in considerable detail with variation of concentration, wave-length, light intensity, and temperature.

(2) The experimental results obtained are summarised at the beginning of the discussion in Part II. They include the establishment of the fact that, with high ozone concentrations and a low rate of absorption of light, a reaction chain is set up.

(3) A mechanism is proposed which takes account of practically all the experimental data. An essential part is ascribed in this mechanism to the walls of the containing vessel.

(4) The corresponding thermal reaction is briefly considered in the light of the newly established facts.

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