

#### 412. *The Decomposition of Ozone Photosensitised by Chlorine.*

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THE decomposition of ozone photosensitised by chlorine has been the subject of much study since its discovery by Weigert (*Z. Elektrochem.*, 1908, **14**, 591), who found that no permanent formation of chlorine oxides results and that the rate of increase of pressure remains constant throughout, the decomposition thus appearing to be of zero order with respect to ozone. Bonhoeffer (*Z. Physik*, 1923, **13**, 94), using ozonised oxygen (as also did Weigert), found the quantum yield of the reaction to be 2.

Attempts by Allmand (*e.g.*, *Trans. Faraday Soc.*, 1926, **21**, 603) and others to devise reaction schemes involving chlorine molecules excited by the absorption of radiation were abandoned when the hypothesis became generally accepted that chlorine molecules are dissociated into atoms by ultra-violet light, and a satisfactory explanation of this reaction has not yet been reached. Recent work has, indeed, shown that the reaction kinetics are more complicated than was at first supposed; Allmand and Spinks (*J.*, 1931, 1652; 1932, 599), for instance, working with ozone purified by fractional distillation, found (1) values of quantum yield greatly exceeding 2, (2) that chlorine hexoxide may separate as a mist, and (3) that there is evidence of a non-linear relation between reaction velocity and absorbed light flux.

The present work was undertaken with a view to investigate the effect of inert gases added to the ozone-chlorine mixture, as in the decomposition of nitrogen trichloride; the latter reaction is also photosensitised by chlorine, is strongly influenced by inert gases, and resembles the ozone reaction in being of zero order with respect to nitrogen trichloride (Griffiths and Norrish, *Proc. Roy. Soc.*, 1931, **130**, *A*, 591; 1932, **135**, *A*, 69), but in this instance the reaction rate is proportional to the absorbed light flux.

#### EXPERIMENTAL.

*Preparation of Reagents.*—Chlorine, prepared from hydrochloric acid and potassium permanganate, was bubbled through potassium permanganate solution, dried, and condensed in liquid air; several fractionations were then carried out. Chlorine from a cylinder, treated in the same way, was also used.

Oxygen was prepared by electrolysis of aqueous caustic soda containing a little baryta, or by the decomposition of hydrogen peroxide; it was stored over mercury under slight pressure.

Nitrogen and carbon dioxide were obtained from commercial cylinders; the former was passed over red-hot copper, dried, and stored as for oxygen, and the latter was condensed and fractionated four or five times. Chlorine and carbon dioxide were stored as solids, cooled by liquid air.

Ozone of high concentration (*ca.* 90%) was prepared by the method of Riesenfeld and Schwab (*Ber.*, 1922, 55, 2088). Oxygen, obtained by the first method above, was partly dried with sulphuric acid, passed through an electrically heated furnace containing platinised asbestos at 350° in order to remove any traces of hydrogen, and then thoroughly dried with calcium chloride and phosphoric oxide before entering the ozoniser. This (Fig. 1a) consisted of three Berthelot tubes in series, each 25 cm. long, and with an annular space 0.2 cm. in width. An alternating current of 500 cycles per second was obtained from a small "Newton 52a" alternator, delivering 20 amps. at 10 volts, and transformed to a potential of 10,000 volts. The

FIG. 1a.  
Preparation of ozone.

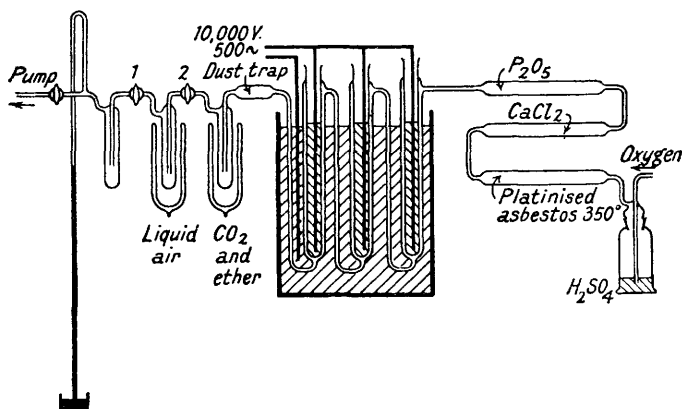
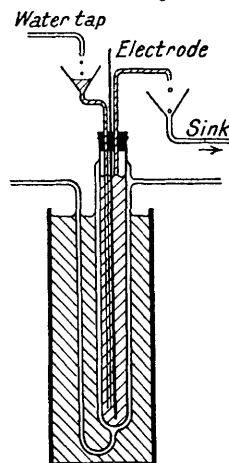


FIG. 1b.  
Detail of ozoniser showing cooling system.



ozoniser was cooled by allowing water to flow through the inner tube. Owing to the need for complete insulation of the high-voltage system, the water was arranged to drip in and out of the tube (see Fig. 1b). The ozoniser stood in a large jar of copper sulphate solution which served as one electrode, the cooling water being the other; it gave approximately 8% of ozone by volume. The mixed ozone and oxygen then passed through a dust-trap, consisting of a glass tube filled with glass-wool moistened with concentrated sulphuric acid, through a trap cooled in carbon dioxide-ether, where the last traces of water were removed (when first used, the walls of the ozoniser tubes gave up much water under the influence of the discharge), and then through a trap cooled in liquid air, where concentration of the ozone took place.

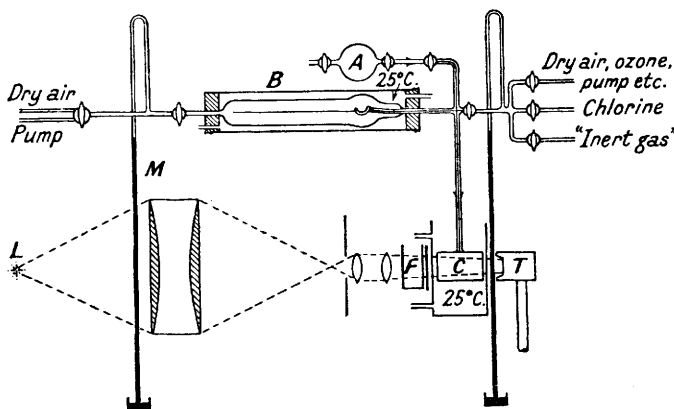
It was found convenient to use a continuous flow method, whereby the oxygen was drawn through the ozoniser at a rate of about 200 c.c./min., the pressure in the liquefying trap being adjusted to 10 or 15 cm. Hg by means of taps (1) and (2) (Fig. 1a). The pressure of the gas in the trap was indicated by a mercury manometer, the surface of which was effectively protected from ozone by a layer of sulphuric acid. Under these conditions, a dark blue liquid containing 70% ozone and 30% of oxygen was condensed. This could be kept indefinitely without decomposition, but explosions occurred if the ozone was allowed to evaporate and escape into the air through a tube containing soda-lime, recommended by Riesenfeld and Schwab as a means of decomposing surplus ozone. Accordingly, the use of this substance was abandoned and ozone rejected, if necessary, through a filter-pump. In order to obtain ozone of greater concentration than 70%, the blue solution was allowed to warm, and the first portions of the distillate were rejected; the fraction remaining now contained 90% of ozone. Shell Apiezon grease "L" was used to lubricate the taps and appeared to be only slightly affected by ozone.

*Procedure.*—The photochemical decomposition of ozone is accompanied by a thermal decomposition. Bonhoeffer and Allmand counterbalanced this with the help of a duplicate

vessel which was not illuminated, but Kistiakowsky studied the thermal reaction separately, and this method was adopted in the present instance. This is facilitated by the fact that the thermal decomposition of ozone in presence of chlorine shows a very marked induction period (Bodenstein, Padelt, and Schumacher, *Z. physikal. Chem.*, 1929, B, 5, 209). In the present work, measurements of quantum yield were only made during such induction periods and, except under certain conditions indicated below, there was no further increase of pressure after the light was cut off.

The decomposition was carried out (Fig. 2) in a cylindrical quartz cell connected to a glass Bourdon gauge, by which the increase of pressure was measured. Energy measurements were made with a Moll thermopile in conjunction with a Broca galvanometer. The gauge (the deflexion of which was measured by a travelling microscope) was calibrated against mercury manometers, and the thermopile-galvanometer system by means of a carbon-filament lamp whose emission had been measured at the National Physical Laboratory. The sensitivity of both was verified at intervals. Both gauge and reaction vessel were kept at constant temperature by a stream of water from an electrically controlled thermostat, pumped to a constant head and

FIG. 2.  
The reaction system.



- A. Bulb filled with reaction mixture and afterwards detached for analysis of contents.  
 B. Bourdon gauge, used (a) for measurement of small pressures by deflexion; (b) for measurement of pressures of gases in reaction vessel by null method, in conjunction with manometer M.  
 C. Reaction vessel in tank with glass windows. The representation of the optical system is purely diagrammatic.  
 L. Mercury lamp taking 2.5 amps. at 150 volts from D.C. mains.  
 F. Light filters, e.g., 3 cm. 6% solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with a Wratten 18a filter, transmitting  $\lambda 365 \mu\text{m}$  only.  
 T. Thermopile.

allowed to flow back (1) through an outer jacket surrounding the gauge and (2) through a tank with glass windows containing the reaction vessel. The temperatures of both gauge and reaction vessel were maintained in this way at  $25^\circ \pm 0.05^\circ$ . The reaction vessel was first evacuated, and the incident light flux measured. Chlorine was then admitted, followed by ozone and any other gases necessary. The transmitted light was measured after a steady rate of reaction had been reached, and the corrections for reflexion losses, etc., were determined by direct measurement and were represented by a factor of 1.27.

Light of wave-length  $365 \mu\text{m}$  was used throughout the experiments. This was obtained from a mercury-vapour lamp, using a Wratten No. 18A colour filter combined with a 3-cm. layer of 6% copper sulphate solution to remove heat rays.

*General Course of the Reaction.*—The graph of pressure plotted against time was of the type described by previous writers: an immediate small increase of pressure—the Budde effect—was followed by a short induction period during which the rate of the pressure change rose to a steady value, which persisted during the greater part of the reaction, but was followed by an abrupt increase at the end. Quantum yields were measured during the period of constant velocity.

In many cases the quantum yield was measured as soon as the rate of increase of pressure became steady, and before all the ozone was decomposed. In such experiments a bulb was

filled at the same time as the reaction vessel; this was subsequently detached, and the contents displaced through a solution of potassium iodide, the sum of the chlorine and ozone pressures being obtained by titration of the iodine liberated after acidification. In other experiments, in which only a small amount of ozone was used, this was estimated from the final increase of pressure.

It was not possible to follow the photosensitised decomposition of more than 5–10 mm. of ozone, but the initial rate of decomposition was found to vary when the concentration of ozone was varied widely. In general the "induction period" and "final rise" were less marked when more oxygen was present, while increase of chlorine had the opposite effect.

Fig. 3 shows typical pressure–time curves. It will be noted that the addition of oxygen, while lowering the quantum yield, does not destroy the characteristic zero order of the reaction with respect to ozone. In one instance (Curve 1), the experiment was interrupted, and apart from the reversible Budde effect, no after-effects occurred.

*The Effect of Variation in Pressure of Chlorine, Pressure of Ozone, and Intensity of Light.*—The effects of variation of these three factors were seen to be closely interconnected. As found by Allmand and Spinks (*loc. cit.*), it was confirmed that with either reduction of chlorine pressure or increase of ozone pressure there was a tendency to approximate to the law  $\gamma \propto I_{\text{abs.}}^{0.75}$ .

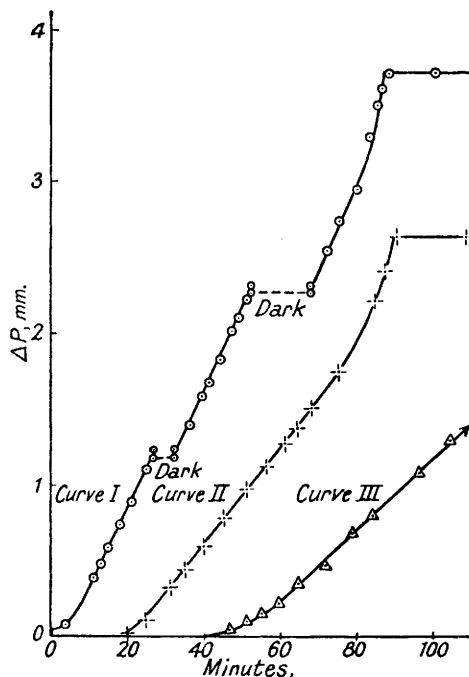
If the pressure of chlorine exceeded approximately 120 mm. a liquid deposit settled on the walls of the cell. A considerable quantity of this liquid was collected by the illumination of a mixture rich in chlorine and ozone, cooled in ice and salt. On allowing the red liquid to become warm, spontaneous decomposition set in, as indicated by an increase of pressure, the rate being rapid but measurable at 30°. On further cooling by ice and salt, it was found that permanent gases had been produced. A quantity of the liquid was condensed in an evacuated bulb, sealed off, and analysed by the method of Schumacher and Stieger (*Z. anorg. Chem.*, 1929, 184, 272). The liquid was decomposed completely by immersing the bulb in hot water and the chlorine and oxygen produced were determined, the former by titration, the latter by volume. In this way the formula  $(\text{ClO}_3)_n$  was established. This trioxide can probably be identified with the oxide described by Bowen (*J.*, 1923, 123, 2328), by Bodenstern, Harteck, and Padelt, and by Schumacher and Stieger (*loc. cit.*). Its formation and thermal decomposition were reported by Allmand and Spinks (*loc. cit.*), and in our opinion it is responsible for the "anomalous" results recorded at high pressures of chlorine and ozone by Heidt, Kistiakowsky, and Forbes (*J. Amer. Chem. Soc.*, 1933, 55, 223). We have already elaborated this point (*Nature*, 1933, 131, 544).

Table I and Figs. 4 and 5 show the effect of variations of pressure of (a) chlorine, (b) ozone with simultaneous variation of absorbed light flux, effected by variation of lamp voltage and by the use of filters of varying transmission. The intensity of absorbed light,  $I_{\text{abs.}}$ , is given in terms of quanta/sec., and pressures of gases in mm. of Hg.

*The Effect of Gases other than Ozone and Chlorine.*—Experiments of two types were made in order to determine the effect of the addition of certain gases.

(a) The quantum yield was determined for two series of mixtures containing severally 60 mm. and 100 mm. of chlorine, with 5–10 mm. of ozone and a varying quantity of a third gas. Under

FIG. 3.  
Typical pressure–time curves.



(Curves II and III are displaced to the right by 20 and 40 minutes respectively.)

	Cl <sub>2</sub> , mm.	O <sub>3</sub> , mm.	O <sub>2</sub> , mm.	I <sub>abs.</sub> , × 10 <sup>-14</sup> .	γ.
Curve I	60	7.5	7	13.0	8.53
„ II	60	5.3	16	7.54	3.59
„ III	60.5	5	635	7.72	2.62

these conditions the quantum yield was found to be independent of absorbed light flux, and the reaction was of zero order with respect to ozone.

TABLE I.

Cl <sub>2</sub> .	O <sub>3</sub> .	O <sub>2</sub> .	I <sub>abs.</sub> × 10 <sup>-14</sup> .	γ.	Cl <sub>2</sub> .	O <sub>3</sub> .	O <sub>2</sub> .	I <sub>abs.</sub> × 10 <sup>-14</sup> .	γ.
<i>Variation of chlorine pressure.</i>									
5.8	39	4.5	1.14	6.1	28.8	36	5	5.31	3.52
			0.919	6.1				4.05	3.82
			0.472	8.2				1.93	4.5
			0.344	9.8				1.55	4.53
14.2	34	6.5	3.26	2.7	55.5	36	5	7.33	3.1
			2.52	3.12				5.62	3.11
			1.81	3.27				3.09	3.16
			1.04	3.85					
			0.69	5.4					
<i>Variation of ozone pressure.</i>									
25.2	5	10	5.15	3.86	25	69	10	5.6	5.22
			4.02	3.84				3.8	5.27
			2.16	4.14				2.1	6.43
22.5	32	4.5	3.87	4.4				1.59	7.63
			2.95	4.47					
			1.64	5.22					
			1.18	5.8					

(b) The variation of quantum yield with absorbed light flux was studied, using 25 mm. of chlorine, 75 mm. of ozone, and either 0 or 600 mm. of a third gas. It was found that nitrogen

FIG. 4.

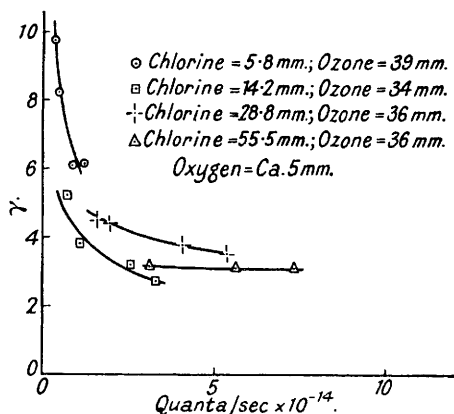


FIG. 6.

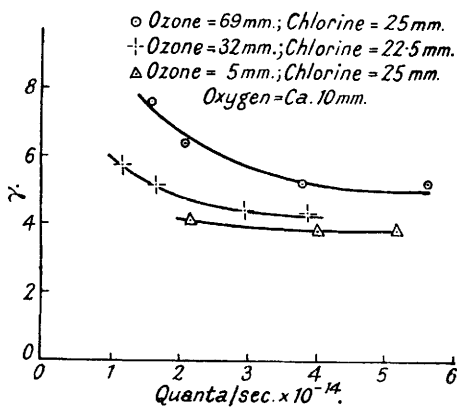
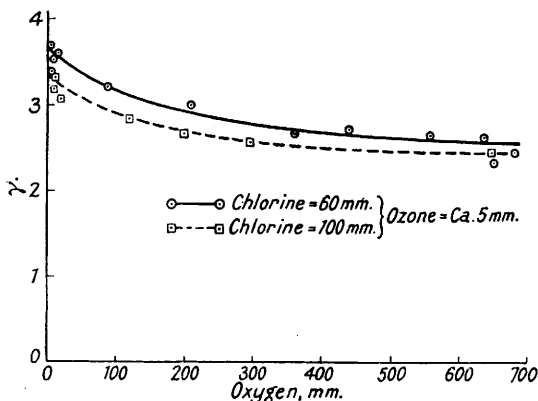


FIG. 5.

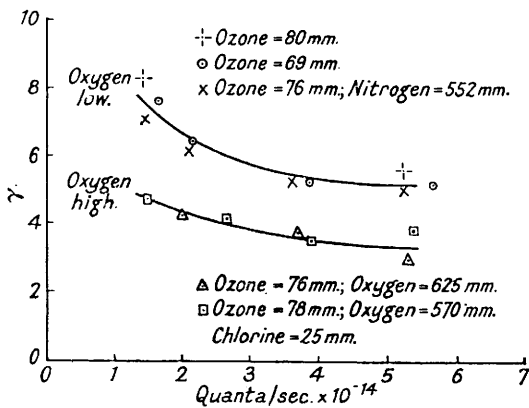


FIG. 7.

and carbon dioxide had no effect on  $\gamma$ , whereas oxygen and chlorine have a marked inhibitory effect, the addition of either of the last two gases tending to obliterate the variation of quantum yield with absorbed light flux and also to reduce the quantum yield.

Oxygen prepared from hydrogen peroxide had the same effect as that produced by electrolysis, and substitution of a small quartz cell for the large one generally used did not affect the quantum yield. It was also found that variation of the total illuminated surface had no effect, a special reaction vessel having movable vanes, which could be swung into the beam, being used for this purpose. Tables II and III exhibit these results, which are plotted in Figs. 6 and 7.

TABLE II.

Experiments with chlorine and ozone at constant pressure, under conditions such that quantum yield is independent of absorbed light flux.

(a) Addition of oxygen.					
Cl <sub>2</sub> , 60 mm.; O <sub>3</sub> , ca. 5 mm.			Cl <sub>2</sub> , 100 mm.; O <sub>3</sub> , ca. 5 mm.		
O <sub>2</sub> .	$\gamma$ .	O <sub>2</sub> .	$\gamma$ .	O <sub>2</sub> .	$\gamma$ .
5.5	3.67	89	3.2	550	2.65
5.5	3.39	124	3.08	635	2.62
6	3.68	210	2.99	650	2.34
8.5	3.54	360	2.67	680	2.44
16	3.59	440	2.71		

(b) Addition of nitrogen.			(c) Addition of carbon dioxide.		
Cl <sub>2</sub> , 60 mm.; O <sub>3</sub> , ca. 5 mm.			Cl <sub>2</sub> , 55 mm.; O <sub>3</sub> , ca. 30 mm.		
N <sub>2</sub> .	O <sub>2</sub> .	$\gamma$ .	CO <sub>2</sub> .	O <sub>2</sub> .	$\gamma$ .
0	10	3.52	0	8.5	3.69
189	21	3.38	50	13	3.73
545	32	3.25	456	17	3.57

TABLE III.

Experiments with chlorine and ozone at constant pressures under conditions such that quantum yield is not independent of absorbed light flux.

O <sub>3</sub> , 69 mm. O <sub>2</sub> , 10 mm.		O <sub>3</sub> , 78.3 mm. O <sub>2</sub> , 570 mm.		O <sub>3</sub> , 76 mm. N <sub>2</sub> , 552 mm.		O <sub>3</sub> , 80 mm. O <sub>2</sub> , 6 mm.		O <sub>3</sub> , 76 mm. O <sub>2</sub> , 625 mm.	
$I_{\text{abs.}} \times 10^{-14}$ .	$\gamma$ .	$I_{\text{abs.}} \times 10^{-14}$ .	$\gamma$ .	$I_{\text{abs.}} \times 10^{-15}$ .	$\gamma$ .	$I_{\text{abs.}} \times 10^{-14}$ .	$\gamma$ .	$I_{\text{abs.}} \times 10^{-14}$ .	$\gamma$ .
5.6	5.22	5.31	3.85	5.17	5.08	5.17	5.68	5.24	2.99
3.8	5.27	3.84	3.55	3.52	5.37	1.38	8.3	3.66	3.74
2.1	6.43	2.57	4.18	2.05	6.2			1.97	4.38
1.59	7.63	1.45	4.67	1.39	7.09				

Note.—The ozone pressures tabulated are those at the commencement of a series of measurements, which were carried out as quickly as possible and without decomposing more than ca. 5% of this ozone. In order to minimise the error due to this, the various intensities used were not studied in the order in which they are tabulated, but in an irregular order as regards magnitude.

### DISCUSSION.

The main points emerging from the present work are as follows :

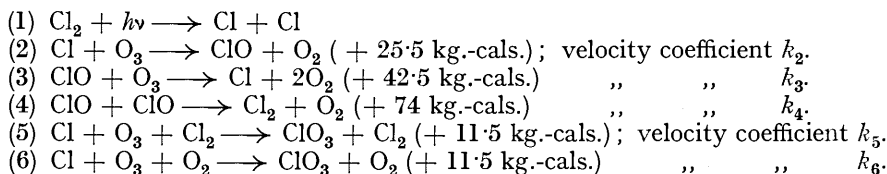
(a) The decomposition of ozone in presence of chlorine is a chain reaction, quantum efficiencies as high as 10 being recorded. (b) The law  $\gamma \propto I^{-0.5}$  is approached when the pressure of ozone is high and that of chlorine and oxygen is low. (c) When the pressure of chlorine or of oxygen is high the quantum yield is independent of absorbed light flux, and the reaction is of zero order with respect to ozone over the greater part of its course. (d) As the pressure of oxygen or chlorine is increased, the light intensity remaining constant, the quantum yield is depressed towards a limiting value of 2. (e) Foreign gases have no effect upon the reaction. (f) A red liquid consisting of chlorine trioxide may be obtained as a by-product when the pressures of chlorine and ozone are high. (g) When chlorine trioxide does not separate, results are uniform and reproducible, and there is no indication of any after-effect when the irradiation is discontinued; if, however, chlorine trioxide separates, it continues to decompose with increase of pressure in the dark.

These results amplify those of earlier workers. It is apparent from the work of Allmand and Spinks (*loc. cit.*) that the apparently simple results of Weigert and of Bonhoeffer (*loc. cit.*) only apply when a large excess of oxygen is present, and that the kinetics are more complicated when a wider range of concentrations of reactants is studied. The first two authors recorded quantum yields as high as 40 when the concentration of ozone was high and that of oxygen low, and under these conditions they found that the velocity is proportional to the square root of light intensity. They also inferred the separation of chlorine trioxide when the pressure of chlorine and ozone was high. With all these results our own findings are in agreement, and in addition we have now recorded the specific inhibiting effect both of oxygen and of chlorine, which is coupled with the fact that, as the pressures of chlorine and oxygen increase, the rate becomes proportional to light intensity. This specific effect of oxygen and chlorine is the more remarkable in view of the absence of any effect by foreign gases.

*Mechanism of Reaction.*—In view of the high quantum yields, it is clear that the decomposition of ozone must occur by way of a chain reaction. Any such chain mechanism must necessarily conform to the following requirements :

(a) At low pressures of chlorine and oxygen, chains end by mutual neutralisation, giving rise to the law  $\gamma \propto I^{-0.5}$ ; in this region the order of reaction is not zero, since the rate is dependent on the concentration of ozone. (b) At higher pressures, chains end by reaction of the active centres with ozone and either chlorine or oxygen: only in this way can the reaction become of zero order and subject to inhibition by chlorine or oxygen. (c) When chains end by self-neutralisation they must do so through the mutual reaction of radicals and not atoms, for in the former instance only can the process be independent of an inert-gas effect. (d) Since chlorine trioxide is formed in greatest quantity under conditions of inhibition by chlorine, *i.e.*, when quantum yield is approaching 2 and the rate is proportional to absorbed light flux, it may be concluded that the radical  $\text{ClO}_3$  is not a chain carrier, as supposed by Allmand and Spinks (*loc. cit.*), but is rather the end-point in the chain reaction when chains are ended by the specific action of chlorine. Moreover if  $\text{ClO}_3$  were also the end-point when the reaction is inhibited by excess oxygen instead of chlorine,  $\text{Cl}_2\text{O}_6$  would not necessarily separate as a liquid, since the absorbed light flux in these experiments was smaller on account of the lower concentration of chlorine employed. Further if chlorine trioxide were the product of the mutual neutralisation of chains, its separation would be expected to be coupled with a  $\gamma \propto I^{-0.5}$  relationship, whereas according to our results this is definitely not the case.

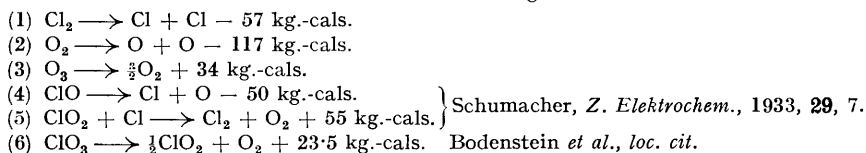
The following scheme fulfils the requirements enumerated above.\*



Of these reactions (1) starts chains, (2) and (3) propagate chains and are strongly exothermic, (4) terminates chains by mutual reaction leading to a  $\gamma \propto I^{-0.5}$  law and is strongly exothermic, and (5) and (6) terminate chains by the specific inhibitive action of chlorine and oxygen leading to a zero-order reaction and the formation of chlorine hexoxide.

The greatest difficulty is to account for the specific inhibitive action of chlorine and oxygen. The experimental results are clear as to its existence, and equally clear as to the

\* The heats of reaction are calculated from the following data :



absence of any inert-gas effect with either nitrogen or carbon dioxide. It must therefore be admitted that the chlorine and oxygen do not exert their influence simply through the mechanism of a ternary collision. It seems possible that their specific action is connected with the formation of  $\text{Cl}_3$  and  $\text{ClO}_2$ . The existence of the former as a transient compound has been shown to be probable by Eyring and Rollefson (*J. Amer. Chem. Soc.*, 1932, **51**, 170) on the basis of wave-mechanical considerations. Hence the reaction  $\text{Cl} + \text{Cl}_2 \longrightarrow \text{Cl}_3$  may be regarded as strongly reversed.

Similarly, Bodenstein (*Trans. Faraday Soc.*, 1931, **27**, 414) has indicated that the direct reaction between chlorine atoms and oxygen molecules to give chlorine dioxide is extremely inefficient, being subject to a probability factor as low as  $10^{-6}$ . Hence the reaction  $\text{Cl} + \text{O}_2 \longrightarrow \text{ClO}_2$  is also strongly reversed. If, however, during their short lives the transient molecules  $\text{Cl}_3$  or  $\text{ClO}_2$  encounter an ozone molecule, they may react as follows:  $\text{Cl}_3 + \text{O}_3 \longrightarrow \text{ClO}_3 + \text{Cl}_2$ ;  $\text{ClO}_2 + \text{O}_3 \longrightarrow \text{ClO}_3 + \text{O}_2$ . For the latter reaction there is independent evidence, since it has been shown by Bodenstein, Harteck, and Padelt (*loc. cit.*) that chlorine dioxide and ozone react to give chlorine trioxide. In this way justification for the reactions (5) and (6) may be given, since the above processes are kinetically equivalent to ternary collisions.

The scheme of reactions given above readily leads to the following kinetic expressions for the velocity of decomposition of ozone, and for the quantum yield.

(1) With low oxygen, low chlorine and high ozone concentrations, when reaction (4) predominates as a chain-ending mechanism:

$$\begin{aligned} -d[\text{O}_3]/dt &= 2I_{\text{abs.}} + 2\sqrt{2/k_4} \cdot k_3[\text{O}_3]\sqrt{I_{\text{abs.}}} \\ \gamma &= 2 + 2\sqrt{2/k_4} \cdot k_3[\text{O}_3]/\sqrt{I_{\text{abs.}}} \end{aligned}$$

(2) With high oxygen or chlorine and low ozone concentrations, when reactions (5) and (6) predominate as chain-ending mechanisms:

$$\begin{aligned} -d[\text{O}_3]/dt &= 2I_{\text{abs.}} + 4k_2I_{\text{abs.}}/(k_6[\text{O}_2] + k_5[\text{Cl}_2]) \\ \gamma &= 2 + 4k_2/(k_6[\text{O}_2] + k_5[\text{Cl}_2]) \end{aligned}$$

The second of these two expressions reduces in the limit to the simple results of Bonhoeffer and of Weigert (*loc. cit.*). Together they fulfil qualitatively all the requirements enumerated above, and are in agreement with the results of Allmand and Spinks. It is not possible, however, to apply any closer quantitative verification, because, except under limiting conditions, the experimental results necessarily lie in a region intermediate between the two expressions.

The kinetics of the photosensitised decomposition of ozone, so far as the second expression above is concerned, are closely analogous to those of the decomposition of nitrogen trichloride photosensitised by chlorine (*loc. cit.*). In both these cases the reaction is of zero order, while quantum efficiencies approach limiting values of 2 and are independent of absorbed light flux. There is, further, the resemblance that at the end of the reaction there occurs a marked acceleration. This is to be explained by the fact that, for the zero-order character of the reaction to be preserved, the product of the number of chains ( $n$ ) and the concentration of ozone or nitrogen trichloride must remain constant. Thus at the very end of the reactions, as the concentrations of ozone or nitrogen trichloride sink to zero, the value of  $n$  may rapidly become large. Under these conditions a semi-explosive effect may intervene by the rapid self-destruction of the chain carriers.

*Mechanism of Thermal Decomposition.*—The mechanism described above differs from that suggested by Bodenstein, Padelt, and Schumacher (*loc. cit.*) for the thermal decomposition of ozone sensitised by chlorine, in which they regard the radical  $\text{ClO}_3$  as a chain carrier. We have given our reasons for concluding that this radical does not act in this manner, and if valid, these reasons must also be applicable to the thermal decomposition. There seems no reason why our mechanism should not also apply to the thermal reaction, since it readily yields a kinetic result identical with that of Bodenstein, Padelt, and Schumacher (*loc. cit.*).



Thus, the reaction  $\text{Cl}_2 + \text{O}_3 \longrightarrow \text{ClO} + \text{ClO}_2$ , followed by reactions (3), (2), (4), and  $\text{ClO}_2 + \text{O}_3 \longrightarrow \text{ClO}_3 + \text{O}_2$ , gives for the velocity of decomposition of ozone

$$-d[\text{O}_3]/dt = \text{const.} \times [\text{Cl}_2]^{\frac{1}{2}}[\text{O}_3]^{\frac{3}{2}}.$$

It was supposed by Schumacher and Wagner (*Z. physikal. Chem.*, 1929, *B*, 5, 207) that the radical ClO could not act as a chain carrier since the quantum yield of the photosensitised reaction was believed not to exceed 2. This limitation is now removed, and the present scheme has the merit of combining in one explanation the mechanisms of both thermal and photochemical decompositions.

#### SUMMARY.

The decomposition of ozone, photosensitised by chlorine, has been investigated using light of wave-length  $365 \text{ m}\mu$  at  $25^\circ$ .

With low concentrations of ozone, the reaction is of zero order and has a chain mechanism. At high ozone and low chlorine concentrations, the rate of reaction is proportional to the square root of absorbed light flux, and chains are terminated mainly by self-neutralisation.

With high concentrations of chlorine or oxygen, the rate is proportional to the first power of the absorbed light flux. This change in the kinetics is coupled with specific inhibiting effects of chlorine and oxygen which become apparent at high concentrations of these gases.

Foreign gases have no effect on this reaction.

Liquid chlorine trioxide  $(\text{ClO}_3)_n$  separates as a by-product when the concentration of ozone and chlorine is high. This continues to decompose when the irradiation is discontinued. In circumstances such that the liquid oxide does not separate, the results are uniform and reproducible.

An energetically possible scheme, involving the propagation of chains by chlorine atoms and ClO radicals, is suggested, and is shown to be in agreement with the present results and with those of earlier workers.

The thermal reaction is discussed in its relation to this scheme.

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