178. *The Photosynthesis of Hydrogen Chloride in Oxygen-rich Mixtures: The Quantum Efficiency of Water Formation.*

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THE photo-combination of hydrogen and chlorine may be considered in three main divisions: (*a*) oxygen-free mixtures, (*b*) oxygen-rich mixtures characterised by direct proportionality between rate of reaction and intensity of absorbed light, and (*c*) the "transition region," in which the characteristics of both (*a*) and (*b*) can be related to the amount of oxygen present. In the region (*b*), provided the ratio of chlorine to hydrogen concentrations is not too large, the retarding effect of oxygen is undoubtedly to be ascribed mainly to the removal of the hydrogen atoms of the reaction chains (Norrish and Ritchie, *Proc. Roy. Soc.*, 1933, *A*, **140**, 713; Norrish, *Trans. Faraday Soc.*, 1931, **27**, 461; Krauskopf and Rollefson, *J. Amer.

Chem. Soc., 1934, **56**, 327), and in this connection Norrish and Ritchie (*loc. cit.*) considered as most probable the following mechanism :

$$\mathrm{H} + \mathrm{O_2} + \mathrm{H_2} = \mathrm{H_2O} + \mathrm{OH}$$
$$\mathrm{H} + \mathrm{O_2} + \mathrm{HCl} = \mathrm{H_2O} + \mathrm{ClO}$$
$$\mathrm{H} + \mathrm{O_2} = \mathrm{HO_2}$$

The last equation was taken to represent a straight bimolecular reaction (cf. Bates and Lavin, *J. Amer. Chem. Soc.*, 1933, **55**, 81) ; the rate of hydrogen chloride formation would on this account be independent of the addition of a foreign gas such as nitrogen. On the other hand, Bodenstein and Schenk (*Z. physikal. Chem.*, 1933, *B*, **20**, 420), from a comprehensive study of the quantum efficiencies of both hydrogen chloride and water formation, proposed the scheme

$$\mathrm{H} + \mathrm{O_2} + \mathrm{M} = \mathrm{HO_2} + \mathrm{M} \qquad \mathrm{HO_2} + \mathrm{Cl_2} = \mathrm{HCl} + \mathrm{ClO_2}$$
$$\mathrm{HO_2} + \mathrm{H_2} = \mathrm{H_2O} + \mathrm{OH} \qquad \mathrm{HO_2} + \mathrm{HCl} = \mathrm{H_2O} + \mathrm{ClO}$$

The key reaction is here the stabilisation of the $\mathrm{HO_2}$ complex by a third gas molecule. Nitrogen acting in this capacity would facilitate the removal of hydrogen atoms and thus produce a decrease in the rate of hydrogen chloride photosynthesis. The question is of importance in more than one connection : any system in which hydrogen atoms are produced in an atmosphere of oxygen and hydrogen (*e.g.*, the mercury-sensitised formation of hydrogen peroxide and water) must be capable of representation by suitable modification of the above schemes. That the formation of the $\mathrm{HO_2}$ complex does require a stabilising triple collision has been indicated by other workers (*e.g.*, Farkas and Sachsse, *ibid.*, 1934, *B*, **27**, 111).

Ritchie and Norrish (*Nature*, 1932, **129**, 243) reported that nitrogen had no appreciable effect on the quantum efficiency of hydrogen chloride formation in oxygen-rich mixtures. Their experiments were carried out with comparatively small pressures of nitrogen. The present paper constitutes an extension of these experiments, nitrogen, carbon dioxide, argon, neon, and helium being the gases investigated. The quantum efficiency of water formation may thus be expected to depend similarly on the addition of " inert " gas; measurements were therefore undertaken to determine the mechanism of hydrogen atom removal consistent with both hydrogen chloride and water formation.

EXPERIMENTAL.

(a) *Quantum Efficiency of Hydrogen Chloride Formation* (γ_{HCl}).—Use was made of the photometric method already described (Ritchie and Norrish, *Proc. Roy. Soc.*, 1933, *A*, **140**, 99), the " method of averaging " being adopted. Hydrogen and oxygen were obtained by electrolysis of potassium hydroxide solution, and cylinder chlorine was employed. Purification of these reactants and of the other gases was as already described (Ritchie and Norrish, *loc. cit.*; Ritchie, *ibid.*, 1934, *A*, **146**, 828). The soft-glass vessel, of approximately 35 c.c. volume, was spherical and attached to the Bourdon " sickle " gauge by a ground-glass joint lubricated by Apiezon grease L. Although the material of the reaction vessel may be of great importance in oxygen-free mixtures, where very high quantum efficiencies are to be expected (cf. Potts and Rollefson, *J. Amer. Chem. Soc.*, 1935, **57**, 1027), yet in oxygen-rich mixtures with quantum efficiencies of not more than 150, the effect of such factors appears to become inappreciable. The light source was an ordinary 500-watt lamp, run at 190 volts from 220-volt mains and controlled by a variable hand resistance. The white light from this lamp was employed in the actual photo-combination, and the chlorine concentration at the end of each period of illumination was determined by means of the light produced ($\gamma \doteqdot 3650$ A.) by inserting a plate of Chance's " ultraviolet " glass in the path of the light beam. Values of $\log I_0/I$, where I_0 is the transmitted intensity for zero chlorine pressure and I that for any other pressure, were then obtained by means of the photo-electric cell arrangement already described (Ritchie, *loc. cit.*), and compared with the values obtained by preliminary calibration for various chlorine pressures. The experimental system did not yield directly an exactly linear proportionality between $\log I_0/I$ and chlorine pressure in the range 0—100 mm., but the departure from linearity was small, and readings were sufficiently accurate for the purpose. The temperaure at which all experiments were carried out was 25°.

Results.—Quantum efficiencies $\gamma_{\mathrm{HCl}}^{\mathrm{exp.}}$ were calculated by the formula

$$\gamma_{\mathrm{HCl}}^{\mathrm{exp.}} = k\,.\,2\Delta\,[\mathrm{Cl_2}]/t\,.\,I_{\mathrm{abs.}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where $\Delta[Cl_2]$ represents the decrease in chlorine pressure during the illumination by white light for t minutes, $I_{abs.}$ being the absorbed light expressed in galvanometer scale divisions, and calculated from the data of the chlorine concentration determination. Since the change in chlorine concentration involved was in general the same, and in other respects the light system was unaltered, relative quantum efficiencies are obtained by the above formula, although the actual illumination was carried out with white and not with "ultraviolet" light alone. Direct experiment showed that the addition of the various other gases did not appreciably alter the absorption of 3650 A. light; in view of the fact that the absorption coefficient of chlorine falls off rapidly as the wave-length increases, the use of white light for the actual illumination was not regarded as requiring in this connection any additional correction. In Table I are given details of a series of experiments on the variation of hydrogen pressure, the initial pressures of the other reactants being approximately the same in each experiment. In this and the following tables, $[Cl_2]$, $[HCl]$, etc., represent the average concentration of reactants during the illumination; in all experiments where values of γ_{HCl} are recorded, no hydrogen chloride was present initially and $\Delta[Cl_2] = [HCl]$.

TABLE I.

γ_{HCl} : *Variation of* $[H_2]$.

$[Cl_2] \doteqdot 45$ mm., $[HCl] \doteqdot 10$ mm., $[O_2] \doteqdot 50$ mm.

$[H_2]$, mm.	$[Cl_2]$, mm.	$[O_2]$, mm.	t, mins.	$[HCl]$, mm.	$I_{abs.}$, divs.	$\gamma^{exp.}_{HCl}$.	$\gamma^{calc.}_{HCl}$.	$\gamma^{exp.}_{HCl}/\gamma^{calc.}_{HCl}$.
453·9	45·5	51·3	25·25	8·4	15·1	53·3	53·2	1·00
398·3	45·7	50·7	25·0	8·6	14·2	58·6	59·2	0·99
338·3	45·4	51·1	25·0	10·5	14·9	68·3	64·0	1·06
333·1	46·8	50·4	17·0	7·8	15·6	71·3	69·2	1·03
222·8	45·7	50·7	19·0	9·6	14·8	82·6	84·3	0·98
56·8	45·4	51·0	13·5	10·9	15·0	130·2	134·0	0·97

Values of $\gamma^{exp.}_{HCl}$ were obtained by assigning the value $2{\cdot}43 \times 10^3$ to k in equation (1). $\gamma^{calc.}_{HCl}$ was obtained by means of the equation (Norrish and Ritchie, *loc. cit.*)

$$\gamma_{HCl} = \frac{3{\cdot}77 \times 10^4 \times [H_2] \times [Cl_2]}{[O_2]\{9{\cdot}25([Cl_2] + 1{\cdot}7[HCl]) + [H_2]([H_2] + 4[HCl] + 140)\}} \quad . \quad . \quad (2)$$

In effect, the absolute absorbed energy in these experiments was determined by comparison with the experiments of Norrish and Ritchie. Strictly, equation (2) refers to light of wave-length 3650 A.; this is not regarded as introducing any large error in the calculated "absolute" values for the wave-lengths effective under the above conditions of oxygen-rich mixtures (cf. Ritchie and Norrish, *Nature*, 1932, **129**, 243).

For the conditions in question, the first term of the denominator is small in comparison with the second; the probable error in the coefficient 1·7 (Potts and Rollefson, *loc. cit.*) does not here have appreciable significance. The ratios of the last column of the table confirm the use of equation (2) as an expression of the retarding effect of hydrogen.

Tables II and III give details of those experiments in which various gases were separately added. In all cases such addition resulted in a decreased quantum efficiency.

In the experiments of Table III, a tap was inserted between gauge and reaction vessel to prevent diffusion of chlorine from the non-illuminated gauge during the long time of illumination required for mixtures of high oxygen concentration. In control experiments for the conditions of Tables I and II, however, no difference in rate could be detected whether this tap was open or closed.

(b) *Quantum Efficiency of Water Formation* (γ_{H_2O}).—The method adopted was to introduce a small quantity of phosphoric oxide (B.D.H.) into the reaction vessel, the consequent decrease in pressure on illumination, due to formation and removal of water vapour, being recorded by means of the calibrated telescope-gauge-pointer system. One telescope scale division was equivalent to 0·0835 mm. at the pressures employed, readings being accurate to 0·1 division, *i.e.*, 0·0083 mm. The use of tap grease, and consequent absorption of chlorine and hydrogen chloride, necessitated a correction; this, however, was small in comparison with the total decrease (see Table IV) and was approximately the same both before and after the period of illumination. It was largely to minimise this correction that white light was employed, its use giving a relatively large decrease, due to formation of water, in a reasonable time of illumination. The normal "dark" decrease was not obtained immediately the light was cut off, several minutes being generally required for the complete removal of water vapour from the gas phase. A small graphical extrapolation was therefore used to determine the pressure at the actual end of the

TABLE II.

γ_{HCl} : *Variation of* $[N_2]$, $[CO_2]$, [A], [Ne], *and* [He].

$[[Cl_2] \doteqdot 45$ mm.; $[H_2] \doteqdot 55$ mm.; $[HCl] \doteqdot 10$ mm.; $[O_2] \doteqdot 50$ mm.

Added gas, mm.	$[H_2]$, mm.	$[Cl_2]$, mm.	$[O_2]$, mm.	t, mins.	[HCl], mm.	$I_{abs.}$, divs.	$\gamma^{exp.}_{HCl}$.	$\gamma^{calc.}_{HCl}$.	$\gamma^{exp.}_{HCl}/\gamma^{exp.}_{calc.}$.
				Addition of nitrogen.					
0·0	54·6	46·0	50·4	14·0	12·0	15·35	135·2	136·0	0·99
101·0	55·5	45·5	50·1	15·0	10·9	15·5	113·5	105·5	1·07
221·8	55·5	45·4	51·1	16·0	8·8	15·7	85·0	83·1	1·02
301·2	56·7	47·5	50·4	18·5	9·0	15·4	76·5	76·3	1·00
396·3	56·7	46·4	50·7	20·0	8·5	15·9	64·8	64·7	1·00
451·1	58·3	47·0	51·6	20·0	7·4	15·6	57·6	60·3	0·96
				Addition of carbon dioxide.					
121·0	55·0	45·6	51·0	22·0	9·9	13·6	80·3	75·7	1·06
178·0	54·0	45·2	50·8	28·0	10·5	13·75	66·1	62·0	1·06
230·1	55·9	45·6	50·5	30·0	9·2	14·0	53·1	54·7	0·97
305·3	56·4	46·4	50·9	30·0	8·2	14·3	46·3	46·3	1·00
				Addition of argon.					
101·0	55·3	45·8	50·0	15·0	10·4	14·8	113·6	115·2	0·99
201·0	56·3	45·5	51·2	16·0	9·4	14·65	97·2	101·3	0·96
301·3	54·3	45·3	50·6	19·0	10·6	14·5	93·5	89·7	1·04
399·0	55·9	45·7	50·6	19·0	9·3	14·45	82·3	82·0	1·00
449·6	57·0	46·1	50·5	18·0	8·9	15·2	79·1	79·3	1·00
				Addition of neon.					
0·0	55·1	45·4	49·2	12·0	10·9	15·8	139	139	1·00
181·7	55·2	45·5	50·3	14·5	10·5	14·4	122	118	1·00
263·8	55·3	44·2	51·4	15·0	10·5	15·9	107	106	1·01
302·5	56·7	45·0	50·9	14·0	10·0	16·5	105	106·5	0·99
0·0	55·4	44·4	50·0	13·0	11·0	15·6	131	134	0·98
387·5	57·8	45·5	51·1	16·0	9·7	14·9	98·6	101	0·98
449·9	54·8	45·4	50·3	16·0	10·4	15·85	99·5	98·4	1·01
				Addition of helium.					
0·0	56·0	45·6	50·1	12·0	10·3	15·6	133	139	0·96
247·4	54·7	45·1	51·0	13·0	9·7	15·9	114	115	0·99
321·1	55·2	45·2	50·1	13·0	9·5	15·8	112	113	0·99
395·1	55·0	45·8	50·3	13·0	9·3	15·7	111	109	1·02

illumination. On an average, five experiments were performed before the phosphoric oxide was replaced.

Details are given in Tables IV, V, and VI. In these experiments, the photo-electric cell arrangement was replaced by a Weston photronic cell and mirror galvanometer. The values of $\gamma^{exp.}_{HCl}$ and $\gamma^{exp.}_{H_2O}$ were obtained by the expressions (1) and

TABLE III.

γ_{HCl} : *Variation of* $[O_2]$.

$[Cl_2] \doteqdot 45$ mm.; $[H_2] \doteqdot 55$ mm.; $[HCl] \doteqdot 10$ mm.

$[H_2]$, mm.	$[Cl_2]$, mm.	$[O_2]$, mm.	t, mins.	[HCl], mm.	$I_{abs.}$, divs.	$\gamma^{exp.}_{HCl}$.	$\gamma^{calc.}_{HCl}$.	$\gamma^{exp.}_{HCl}/\gamma^{calc.}_{HCl}$.
55·2	45·6	49·8	15·0	10·3	12·25	136	139	0·98
54·8	45·3	150·5	40·0	10·0	15·2	39·9	39·4	1·01
52·1	44·1	97·2	45·0	13·4	12·2	59·1	61·7	0·96
54·8	45·7	249·6	80·0	9·8	14·8	20·0	20·9	0·96
55·2	44·8	50·9	20·0	11·3	10·5	130	132	0·99
55·2	45·0	201·3	90·0	10·7	10·6	27·2	26·9	1·01
54·7	45·7	252·1	90·0	9·6	12·4	20·8	20·8	1·00
55·8	46·8	298·0	90·0	8·1	12·6	17·3	17·3	1·00
55·7	45·6	50·8	15·0	10·2	12·25	135	137	0·99

$$\gamma^{exp.}_{H_2O} = k \times \tfrac{2}{3} \times [\Delta]/t \times I_{abs.} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

respectively, where $k = 295$, as obtained from the results of Table V, this value representing in effect the calibration of the light system on the basis of Norrish and Ritchie's equation (*loc. cit.*). [This value of k differs from that previously given (p. 859) because the intensity measurements were carried out by means of a photronic and not by a photo-electric cell.] Here $I_{abs.}$ is expressed as on p. 859, and $\frac{2}{3}[\Delta]$ represents the pressure of water, in mm., produced by white light illumination over *t* minutes. $[\Delta] = 0{\cdot}0835\ (\Delta_1 - \Delta_2)$, where Δ_1 is the total and Δ_2 the "dark" decrease in pressure (both in telescope-scale divisions) over the time *t*.

The method of calculation must be modified for the experiments (*f*) and (*g*), where the actual light absorbed cannot be taken as proportional to that absorbed for 3650 A.; $I_{\text{abs.}}$ was here calculated from the simultaneously measured $d[\text{HCl}]/dt$ which is known to be directly proportional to it. γ_{HCl} was determined at the same time as γ_{H_2O} in the experiments denoted by corresponding numbers. That the presence of phosphoric oxide in the reaction vessel did not appreciably affect the results is evident from the figures of Table VI.

It will be observed that γ_{H_2O} increases rapidly with increasing [H_2], and less rapidly with increasing [HCl], [CO_2], [N_2] and [O_2], but is independent of $I_{\text{abs.}}$, and decreases with increasing [Cl_2].

TABLE IV.

Expt.		[Cl_2], mm.	[H_2], mm.	[O_2], mm.	[HCl], mm.	*t*, mins.	$I_{\text{abs.}}$, divs.	Δ_1.	Δ_2.	$\gamma^{\text{exp.}}_{H_2O}$.	$\gamma^{\text{calc.}}_{H_2O}$.	$\frac{\gamma^{\text{calc.}}_{H_2O}}{\gamma^{\text{exp.}}_{H_2O}}$
(*a*) *Variation of* [H_2].												
1		42·8	41·2	40·5	14·3	6·00	8·50	2·30	0·36	0·63	0·65	1·03
2		41·6	53·5	40·0	15·1	6·50	8·10	2·70	0·25	0·76	0·78	1·02
3		42·0	150·0	40·3	14·6	8·00	8·30	5·15	0·16	1·23	1·23	1·00
4		41·7	305·5	40·6	15·0	12·0	8·32	8·90	0·24	1·43	1·51	1·06
5		42·1	510·2	41·0	13·8	14·0	8·05	11·05	0·28	1·57	1·66	1·06
(*b*) *Variation of* [O_2].												
6		42·5	42·9	46·4	14·0	6·00	8·73	2·13	0·12	0·63	0·67	1·07
7		42·9	43·2	49·5	15·5	6·00	12·2	3·00	0·21	0·62	0·68	1·08
8		43·0	43·2	126·8	14·5	15·00	12·2	8·33	0·45	0·71	0·70	0·99
9		44·5	43·8	231·8	13·6	7·00	12·6	4·20	0·28	0·73	0·72	0·99
10		43·5	43·9	304·1	14·0	8·00	12·2	4·95	0·24	0·79	0·75	0·95
11		42·7	43·3	402·2	14·8	9·00	12·4	5·63	0·27	0·79	0·82	1·04
(*c*) *Variation of* [HCl].												
12		42·7	43·5	50·0	13·3	6·00	9·04	2·30	0·18	0·62	0·67	1·08
13		43·4	42·6	49·8	114·7	15·00	9·90	7·95	0·45	0·83	0·81	0·98
14		44·0	44·5	51·2	212·1	7·50	9·70	4·60	0·25	0·99	0·84	0·85
15		44·2	43·0	50·2	316·1	8·50	10·1	5·70	0·34	1·03	0·86	0·83
16		43·1	42·9	50·3	414·1	10·00	9·75	6·95	0·40	1·12	0·875	0·72
(*d*) *Variation of* [N_2].												
	[N_2].											
17	0·0	43·5	43·0	50·6	13·0	5·75	9·40	2·30	0·13	0·66	0·66	1·00
18	202·0	43·2	44·2	50·2	12·7	9·50	9·30	4·35	0·20	0·77	0·77	1·00
19	304·1	44·0	44·4	51·0	12·0	11·0	9·50	5·05	0·11	0·78	0·79	1·01
20	437·0	43·9	42·5	39·1	15·4	13·0	8·80	6·00	0·42	0·80	0·79	0·99
(*e*) *Variation of* [CO_2].												
	[CO_2].											
21	198·1	44·1	43·8	49·5	13·2	14·0	9·55	6·80	0·14	0·82	0·80	0·98
22	399·0	43·8	42·5	49·5	12·6	8·50	9·56	4·30	0·10	0·85	0·83	0·97
(*f*) *Variation of* $I_{\text{abs.}}$.												
23		42·8	44·0	48·0	13·7	6·00	9·35	2·38	0·12	0·66	0·67	1·02
24		44·2	44·3	49·1	12·0	14·0	3·42	2·25	0·42	0·63	0·66	1·04
25		43·3	43·3	50·3	14·2	6·33	8·80	2·55	0·25	0·68	0·68	1·00
26		42·8	43·1	50·3	14·9	15·0	3·95	2·81	0·37	0·68	0·67	0·99
(*g*) *Variation of* [Cl_2].												
27		21·9	41·6	35·3	16·7	14·0	5·00	3·95	0·14	0·92	1·01	1·09
28		64·8	44·9	99·2	12·0	5·50	14·8	3·10	0·27	0·57	0·51	0·90
29		85·2	45·6	150·7	11·5	4·50	25·0	3·42	0·22	0·47	0·42	0·90
(*h*) *Other experiments.*												
	[N_2].											
30	0·0	45·5	300·2	301·8	12·5	9·00	9·40	7·65	0·27	1·44	1·54	1·07
31	289·0	43·4	300·6	50·9	14·0	8·00	9·00	5·90	0·20	1·30	1·57	1·21
32	152·1	43·8	300·0	52·3	11·4	14·0	9·00	10·85	0·10	1·40	1·54	1·10

TABLE V.

γ_{HCl} *in presence of* P_2O_5.

Expt.		$[Cl_2]$, mm.	$[H_2]$, mm.	$[O_2]$, mm.	$[HCl]$, mm.	t, mins.	$I_{abs.}$, divs.	$\gamma^{exp.}_{HCl}$.	$\gamma^{calc.}_{HCl}$.	$\frac{\gamma^{calc.}_{HCl}}{\gamma^{exp.}_{HCl}}$.
6		42·5	42·9	46·4	14·0	6·00	8·73	158	149	0·94
7		42·9	43·2	49·5	15·5	6·00	12·2	125	137	1·09
8		43·0	43·2	126·8	14·5	15·00	12·2	46·7	47·6	1·02
17		43·5	43·0	50·6	13·0	5·75	9·40	142	140	0·99
12		42·7	43·5	50·0	13·4	6·00	9·04	146	139	0·95
13		43·4	42·6	49·8	114·7	15·0	9·90	53·3	51·5	0·97
	$[N_2]$, mm.									
18	202·0	43·2	44·2	50·2	12·7	9·50	9·30	84·5	85·5	1·01
19	304·1	44·0	44·4	51·0	12·0	11·00	9·50	67·7	69·8	1·03
20	437·0	43·9	42·5	39·1	15·4	13·00	8·80	71·4	75·5	1·06
32	152·1	43·8	300·0	52·3	11·4	14·00	9·00	53·3	53·0	0·99
	$[CO_2]$, mm.									
21	198·1	44·1	43·8	49·5	13·2	14·00	9·55	58·2	60·0	1·03

TABLE VI.

γ_{HCl} *in absence of* P_2O_5.

43·4	45·6	42·0	14·9	6·16	8·60	161	164	1·02
43·3	45·5	92·2	12·8	12·1	8·50	73·6	71·0	0·97

DISCUSSION.

The decrease in pressure on illumination in the presence of phosphoric oxide has been attributed to the formation and removal of water vapour alone, no account being taken of the possible formation of other compounds. Illuminated mixtures of chlorine and oxygen showed no appreciable decrease in pressure which could be of importance in this connection. In hydrogen–chlorine–oxygen mixtures the formation of ClO would not involve in itself a decrease in pressure, although this is to be expected for ClO_2; since, however, these substances do not accumulate, they are presumably at once decomposed by illuminated chlorine. Hydrogen peroxide can be isolated under special conditions (Norrish, *Trans. Faraday Soc.*, **1931**, **27**, 461), although again the amount in ordinary circumstances is very small; moreover, this, too, is decomposed by illuminated chlorine (Bodenstein and Schenk, *loc. cit.*). Consequently, it has been assumed that practically all the hydrogen peroxide formed is converted at once into water. The agreement between values of γ_{HCl} in the presence and in the absence of phosphoric oxide (Tables V and VI) seems to show that the use of the oxide is otherwise free from objection, except possibly with high pressures of hydrogen chloride, where a small absorption by "moist" oxide is not unexpected. This would partly be included in the "dark" correction: actually, comparison of calculated and experimental results (Table IV, *c*) shows a tendency which may be ascribed to this absorption. The experimental values of γ_{H_2O} are in this case maximum values, but the divergence does not sensibly affect the following arguments.

The mechanism adopted to represent the formation of hydrogen chloride and water in such oxygen-rich mixtures is as follows:

$$\begin{array}{rcll}
Cl_2 + h\nu & = & Cl + Cl & \dots\dots\dots\dots\dots \; k_1 \\
Cl + H_2 & = & HCl + H & \dots\dots\dots\dots\dots \; k_2 \\
H + Cl_2 & = & HCl + Cl & \dots\dots\dots\dots\dots \; k_3 \\
H + O_2 + H_2 & = & H_2O + OH & \dots\dots\dots\dots\dots \; k_4 \\
H + O_2 + Cl_2 & = & HCl + ClO_2 & \dots\dots\dots\dots\dots \; k_5 \\
H + O_2 + HCl & = & HO_2 + HCl & \dots\dots\dots\dots\dots \; k_6 \\
H + O_2 + M & = & HO_2 + M & \dots\dots\dots\dots\dots \; k_M \\
HO_2 + H_2 & = & H_2O + OH & \dots\dots\dots\dots\dots \; k_7 \\
HO_2 + Cl_2 & = & HCl + ClO_2 & \dots\dots\dots\dots\dots \; k_8
\end{array}$$

M may be oxygen or any of the indifferent gases mentioned in Table II. Application of the usual methods gives

$$\gamma_{\mathrm{HCl}} = k_1 + \frac{2k_1k_3[\mathrm{Cl}_2]}{k_4[\mathrm{O}_2]\left[[\mathrm{H}_2] + \frac{k_5}{k_4}[\mathrm{Cl}_2] + \frac{k_6}{k_4}[\mathrm{HCl}] + \frac{k_\mathrm{M}}{k_4}[\mathrm{M}]\right]} \quad . \quad . \quad . \quad (4)$$

$$\gamma_{\mathrm{H_2O}} = \frac{k_1\left[[\mathrm{H}_2] + \frac{\left(\frac{k_6}{k_4}[\mathrm{HCl}] + \frac{k_\mathrm{M}}{k_4}[\mathrm{M}]\right)}{\left(1 + \frac{k_8}{k_7}\frac{[\mathrm{Cl}_2]}{[\mathrm{H}_2]}\right)}\right]}{\left[[\mathrm{H}_2] + \frac{k_5}{k_4}[\mathrm{Cl}_2] + \frac{k_6}{k_4}[\mathrm{HCl}] + \frac{k_\mathrm{M}}{k_7}[\mathrm{M}]\right]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

As Norrish and Ritchie have shown (*loc. cit.*), expression (4) is not quite correct when the pressure of hydrogen is low, in that the denominator must be increased by a term involving $[\mathrm{Cl}_2]/[\mathrm{H}_2]$. Similar remarks apply therefore to expression (5); for simplicity, however, this correction, amounting to a maximum of about 5% in the final calculated efficiency, has here been omitted.

The efficiencies given in the tables have been calculated by making use of the following values : $k_1 = 2{\cdot}0$, $2k_1k_3/k_4 = 3{\cdot}77 \times 10^4$, $k_6/k_4 = 4{\cdot}00$ (Norrish and Ritchie), $k_{\mathrm{O_2}}/k_4 = 0{\cdot}43$, $k_{\mathrm{Cl_2}}/k_4 = 2{\cdot}64$, $k_{\mathrm{CO_2}}/k_4 = 1{\cdot}65$, $k_{\mathrm{N_2}}/k_4 = 0{\cdot}74$, $k_\mathrm{A}/k_4 = 0{\cdot}43$, $k_{\mathrm{Ne}}/k_4 = 0{\cdot}22$, $k_{\mathrm{He}}/k_4 = 0{\cdot}18$, $k_8/k_7 = 1{\cdot}20$.

The last column of each table shows that experimental results for both γ_{HCl} and $\gamma_{\mathrm{H_2O}}$ are reasonably represented by the above scheme. Expression (4), when applied to the original results of Norrish and Ritchie, gives an agreement between experimental and calculated values which is as good as that shown by their earlier formula. There thus seems little doubt that the action of indifferent gases is directly connected with the stabilisation of the $\mathrm{HO_2}$ complex, and that this does not appreciably react further, under the above conditions, in the propagation of the reaction chains. The fact that oxygen can act as an energy acceptor in this connection means that the rate of hydrogen chloride formation is inversely proportional to the concentration of oxygen in an intermediate region which passes, on the one side, at low oxygen concentrations into the " transition " region, and on the other, to a region where the rate is less than would be expected on the basis of such inverse proportionality.

Table VII shows also relative values of coefficients already determined for other triple collisions, the nitrogen coefficient being taken as unity. These refer to concentrations in mm.

TABLE VII.

Relative Triple Collision Coefficients.

Reaction.	HCl.	$\mathrm{Cl_2}$.	$\mathrm{CO_2}$.	$\mathrm{O_2}$.	$\mathrm{N_2}$.	A.	Ne.	He.	$\mathrm{H_2}$.
1. Br + Br			2·16	1·28	1·00	0·52		0·30	0·85
2. Br + Br			1·38	1·38	1·00	0·64		0·41	0·51
3. I + I			2·72	1·59	1·00	0·58		0·27	0·61
4. Cl + $\mathrm{NCl_3}$		2·24	2·24	1·47	1·00	0·94		0·55	0·55
5. H + $\mathrm{O_2}$	5·4	3·57	2·23	0·58	1·00	0·60	0·30	0·24	1·35
6. O + $\mathrm{O_2}$				0·44	1·00	0·63			
7. O + $\mathrm{O_2}$			2·0	2·0	1·00	0·2		0·4	
8. H + H						0·60	0·22	0·06	0·06

1. Rabinowitch and Wood, *Trans. Faraday Soc.*, 1936, **32**, 907.
2. Ritchie, *Proc. Roy. Soc.*, 1934, *A*, **146**, 828.
3. Rabinowitch and Wood, *J. Chem. Physics*, 1936, **4**, 497.
4. Griffiths and Norrish, *Trans. Faraday Soc.*, 1931, **27**, 451; *Proc. Roy. Soc.*, 1934, *A*, **147**, 143.
5. Present results
6. Ritchie, *Proc. Roy. Soc.*, 1934, *A*, **146**, 848.
7. Schumacher and Beretta, *Z. physikal. Chem.*, 1932, *B*, **17**, 417.
8. Senftleben and Hein, *Ann. Physik*, 1935, **22**, 1. No value for nitrogen was determined : the argon coefficient has here been put equal to 0·60 and the other values calculated accordingly.

In the reactions in which only a simple stabilising collision seems possible, efficiencies fall into a well-defined series $\mathrm{CO_2} > \mathrm{N_2} > \mathrm{A} > \mathrm{Ne} > \mathrm{He}$. On this basis the relatively high efficiency of hydrogen for the HO_2 reaction is then due to the fact that the triple collision between H, O_2, and H_2 does not involve stabilisation of the HO_2 complex. It should be pointed out that the same formula for γ_{HCl} and γ_{H_2O} may be obtained if

$$H + O_2 + H_2 = H_2O + OH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$HO_2 + H_2 = H_2O + OH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

are replaced by, respectively,

$$H + O_2 + H_2 = H_2O_2 + H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4')$$

and

$$HO_2 + H_2 = H_2O_2 + H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7')$$

where the subsequent reaction $H_2O_2 + Cl = ClO + H_2O$ must be taken to represent the chain-ending process which undoubtedly occurs in the presence of hydrogen and nitrogen. That hydrogen peroxide is rapidly removed by illuminated chlorine has been already proved (see p. 862). Present results therefore do not distinguish between reactions (4) and (4′). No values of γ_{H_2O} greater than 2 have here been recorded, even with high concentrations of hydrogen, where mutual recombination of OH radicals might occur with subsequent formation of water. The results of Bodenstein and Schenk confirm this, with one exception which is perhaps due to experimental error, since other experiments with similar concentrations give values less than 2. The results of Krauskopf and Rollefson (*loc cit.*) on the ratio of hydrogen used up in water formation to total hydrogen disappearing on illumination are in agreement with this conception that, if the hydroxyl radical is formed, it does not eventually give water under these conditions. Similarly, Chapman and Watkins (J., **1933**, 744) conclude that the quantum efficiency of water formation may rise as high as 2. If reaction (4) be the true one, the hydroxyl radicals must be effectively removed before a process eventually involving the formation of water can take place. Possibilities are

$$OH + Cl_2 = HCl + ClO - 9{\cdot}5 \text{ kg.-cals.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

and

$$OH + Cl = HCl + O - 2{\cdot}5 \text{ kg.-cals.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

Although reaction (*a*) is more strongly endothermic, reaction (*b*) is probably of less importance here, since its rate depends on the product of two very small concentrations and would involve an $(I_{abs.})^{\frac{1}{2}}$ term in the expression for γ_{HCl}, contrary to experiment.

The triple collision between H, O_2, and HCl appears to be a simple stabilising one, contrary to previous supposition; since $k_{HCl}/k_4 = 4{\cdot}00$, γ_{H_2O} would increase very rapidly with increasing pressures of hydrogen chloride if this triple collision yielded water and ClO. Calculated values of γ_{H_2O} in this series are very sensitive to the value of k_8/k_7, representing the rates of reaction of HO_2 with chlorine and hydrogen: it is to be noted that it differs considerably from the ratio k_5/k_4, although there is no immediate reason why these ratios should be identical. The ratio k_5/k_4 is perhaps liable to greater experimental error than usual in that the experimental arrangements did not permit of its more accurate determination with higher pressures of chlorine. The experimental values of γ_{H_2O} at high chlorine pressures are greater than calculated values; this may be partly due to the formation of ClO_2, for which no allowance has been made.

The thermal data of these reactions have already been discussed by Bodenstein and Schenk (*loc. cit.*, p. 435), who show that reactions (7) and (8) are exothermic if the H + O_2 reaction produces not more than 44 kg.-cals. Table VIII shows the data of the first ten

TABLE VIII.

No.	$[Cl_2]$, mm.	$[H_2]$, mm.	$[O_2]$, mm.	[HCl], mm.	$\gamma^{exp.}_{H_2O}$.	$\gamma^{calc.}_{H_2O}$.	$\gamma^{calc.}_{H_2O}/\gamma^{exp.}_{H_2O}$.
1	103·5	372	202	70·4	0·49	1·28	2·62
2	86·5	332	201	151	1·00	1·37	1·37
3	61·4	285	193	221	1·65	1·53	0·93
4	32·0	256	187	256	1·71	1·69	0·99
5	59·4	432	228	44·4	1·23	1·55	1·26
6	59·7	392	218	90·0	1·23	1·55	1·26
7	41·8	381	220	116	1·99	1·67	0·84
8	28·4	378	218	120	2·58	1·76	0·68
9	26·2	365	212	130	1·68	1·77	1·05
10	29·9	394	223	112	1·27	1·75	1·38

of the 22 experiments carried out by those authors (*loc. cit.*, p. 427) at 60° by a flow method involving no phosphoric oxide in the illuminated vessel. The concentrations have been converted from millimoles/l. to mm.; in the penultimate column are given values calculated by the present formula (5) for γ_{H_2O}.

In view of the experimental error apparently involved, there is a reasonable agreement between $\gamma_{H_2O}^{calc.}$ and $\gamma_{H_2O}^{exp.}$, as shown by the ratios in the last column, which average 1·08 if experiment 1 is ignored. In general, the results of Bodenstein and Schenk are lower than those calculated by the present formula (5), more especially when the $[Cl_2]/[H_2]$ ratio is relatively large; the discrepancy is then due probably to the neglect of the term involving $[Cl_2]/[H_2]$ in the denominator (see p. 863), corresponding to the breaking of the reaction chains by removal of chlorine atoms as well as by removal of hydrogen atoms.

SUMMARY.

Measurements have been made of the relative quantum efficiencies of hydrogen chloride and water formation in certain hydrogen–chlorine–oxygen mixtures. The quantum efficiency of hydrogen chloride formation is reduced by the addition of carbon dioxide, nitrogen, argon, neon, and helium; that of water formation increases with increasing pressure of hydrogen, less rapidly with increasing pressures of hydrogen chloride, oxygen, carbon dioxide, and nitrogen, but is independent of the light energy absorbed and decreases with increasing pressure of chlorine. A mechanism is discussed which is consistent for both hydrogen chloride and water formation, where the actions of hydrogen chloride, oxygen, carbon dioxide, nitrogen, argon, neon, and helium are related to the stabilisation of the HO_2 complex in a triple collision.

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