83. *The Photoexpansion of Chlorine ; the Recombination of Chlorine Atoms.*

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Measurements have been made of the photoexpansion of chlorine under various conditions. Possible processes of recombination of chlorine atoms have been discussed in relation to diffusion and thermal conductivity factors; results are in agreement with the mechanism

$$Cl + Cl_2 + M \longrightarrow Cl_3 + M, \quad Cl_3 + Cl_3 \longrightarrow 3Cl_2.$$

Water vapour in small amounts reduces the photoexpansion very slightly when surface actions are involved.

IN a previous paper (W. Smith, Ritchie, and Ludlam, J., 1937, 1680) the recombination of bromine atoms was discussed in relation to the photoexpansion of bromine vapour under certain conditions. For mixtures of the vapour with other gases, a general treatment was developed, which involved diffusion of bromine atoms to the vessel walls as well as thermal conductivities of the various gas mixtures : relative efficiencies of the added gases in the triple collision process $Br + Br + M \longrightarrow Br_2 + M$ were then obtained, the agreement between such values and those calculated by other means being regarded as good support for the analysis.

Investigation of reactions involving chlorine and chlorine atoms has indicated that the recombination of these atoms does not in general take place by an analogous process. Rollefson and Eyring (*J. Amer. Chem. Soc.*, 1932, **54**, 170) put forward on quantum grounds the mechanism $Cl + Cl_2 \longrightarrow Cl_3$, $Cl_3 + Cl_3 \longrightarrow 3Cl_2$, later adopted by other workers. Craggs, Squire, and Allmand (J., 1937, 1887) also suggested the possibility of the triple collision $Cl + Cl_2 + M \longrightarrow Cl_3 + M$ for the first stage, but no definite experimental evidence seems to be available regarding this mechanism. The question is, however, of importance in view of the fact that overall rates of reactions involving chlorine atoms under similar conditions would then be dependent on the pressures of added gas or of otherwise inert products of reaction. Ritchie and Norrish (*Proc. Roy. Soc.*, 1933, *A*, **140**, 116) gave data to show that in oxygen-free mixtures of hydrogen and chlorine the rate of photocombination was retarded by hydrogen chloride itself, and this apparent effect has been the object of considerable investigation and discussion (*inter alios*, Craggs, Squire, and Allmand, *loc. cit.*; Potts and Rollefson, *J. Amer. Chem. Soc.*, 1935, **57**, 1027); recent experiment has favoured the view that any possible effect of hydrogen chloride is connected with surface action only. Since the analysis of the Budde effect in bromine involved consideration of surface effects as well as the kinetics of the atomic recombination in the gas phase, a similar examination of the Budde effect in chlorine is here described.

EXPERIMENTAL.

The apparatus used was similar to that already described (W. Smith, Ritchie, and Ludlam, *loc. cit.*). The glass insolation vessel was of approximately 1500 c.c., the source of light being a 200-watt Osira mercury-vapour lamp, run at 220 volts (variation in voltage less than 1% assured by the use of a Solus stabiliser). The light thus produced passed through a 5% solution of copper sulphate before entering the reaction vessel; the Budde effect observed with the necessary low pressure of chlorine (50 mm.) in conjunction with the most sensitive Bourdon gauge available was too small to permit of monochromatic light being used. A photronic cell–galvanometer arrangement was employed to determine changes in absorbed light. After passing through alkaline permanganate, concentrated sulphuric acid, and over phosphoric oxide, cylinder chlorine was fractionated several times by means of liquid air, being kept normally in the solid state. Cylinder nitrogen, oxygen, and argon were passed through phosphoric oxide and liquid-air traps before use. Carbon dioxide was prepared from calcium carbonate and hydrochloric acid, and purified by successive treatments with sodium carbonate, concentrated sulphuric acid, phosphoric oxide, and carbon dioxide–ether. Similar results were obtained with cylinder carbon dioxide subjected to similar treatment. Hydrogen chloride was prepared from the concentrated acid and concentrated sulphuric acid and purified by fractionation by means of liquid air; identical results were given by the use of hydrogen chloride prepared by illumination of hydrogen (prepared by electrolysis) and chlorine in the reaction vessel itself, this second method being used in an attempt to minimise the effect of possible impurities.

All experiments were carried out at 25°, the temperature being kept constant by a water thermostat.

Procedure.—The system was evacuated by a Hyvac oil pump, and the transmitted light intensity, I_0, at zero pressure of chlorine measured by the photronic cell system. The levels of the mercury manometer and the initial position of the gauge pointer were observed. After the reaction vessel had been washed out with chlorine, this gas was introduced to a pressure of 50 mm., and illuminated under the standard conditions; the deflections of the gauge pointer and the galvanometer mirror spot were recorded. Similar measurements were made for mixtures of chlorine (50 mm.) and various pressures of the added gases, *viz.*, nitrogen, argon, hydrogen chloride, carbon dioxide, and oxygen. Sufficient time was allowed for complete mixing.

RESULTS AND DISCUSSION.

A series of observations not recorded in the corresponding experiments on the Budde effect in bromine vapour is first discussed. In certain mixtures, the initial illumination caused a rise in pressure, the gauge pointer rising to a maximum, which, however, was not maintained, a slightly smaller steady value being finally reached. Similarly, when the light was cut off, the pressure shown by the pointer reached a value slightly less than the original "dark" pressure, this "dark" pressure being, however, again attained after a short period of time. For a given gas mixture, the differences between the "steady" pressures and the corresponding maximum and minimum were sensibly the same; the times concerned in the development of the maximum effects varied with the gas mixture, but were of the same order, *e.g.*, 30 secs. for $[Cl_2] = 50$ mm. and $[N_2] = 300$ mm. The smallness of the effect rendered accurate observation difficult, but maximum differences (dp) were determined for various gas mixtures; results for nitrogen were as follows, dp being given in telescope scale divisions.

$[Cl_2] = 50{\cdot}0$ mm.

$[N_2]$, mm.	0	100	200	300	400	500	600
dp	0·0	0·2	0·4	0·7	0·5	0·2	0·0

The effect is at its greatest at an intermediate pressure of nitrogen, but is negligible at low and at high pressures. Similar results were recorded for argon and oxygen, but were not observed for hydrogen chloride and carbon dioxide.

It is unlikely that the cause of these effects is connected with a rise or fall in temperature of the main body of the gas. It seems more probable that some species is produced as a result of illumination which in the steady state of illumination is adsorbed to some extent on the walls of the vessel; the pressure increase of the "steady" state is then less than the value which would be recorded if no such adsorption occurred.

Correspondingly, when the light is cut off, the pressure falls to a value less than the original pressure, which it only reaches when the adsorbed product escapes into the gas phase. The effect is negligible at zero pressure of added gas; adsorption of chlorine atoms is thus not regarded as responsible, since the number of atoms then reaching the wall will be at its maximum. The species must then become increasingly important as " inert " gas is added to prevent chlorine atoms reaching the wall by diffusion. At the highest pressures of inert gas employed, the species itself may be regarded as prevented from reaching the wall by the inert gas; it does not accumulate but is removed in the gas phase. Such observations indicate that the processes occurring in illuminated chlorine are essentially different from those in illuminated bromine. It is obvious that the Cl_3 molecule visualised in the alternative mechanism might play the part of the adsorbed species assumed to explain this abnormality of the Budde effect; a detailed analysis of each possible process was therefore undertaken.

In view of the above " adsorption effect," the true Budde effect is not the difference between the original dark pressure and the pressure in the steady state of illumination, but rather the change in pressure which would have been observed if no adsorption had occurred. The maximum pressure difference observed was therefore taken as the Budde effect. This value will be somewhat less than the true increase, as adsorption or desorption must be taking place even in the short time taken for this difference to reach this maximum value. The error thus introduced is regarded as small, since the adsorption effect is, at its maximum, about 10% of the total pressure change. Budde effects (Δp) are given in the following tables as divisions of the telescope scale, with an approximate error of $\pm 0{\cdot}1$ div. (1 div. = 0·0486 mm.).

In the examination of each mechanism, chlorine atoms are taken to be formed as the direct result of absorption of light of the wave-lengths transmitted by the system.

Mechanism (1) : $Cl + Cl + M \longrightarrow Cl_2 + M$.—Application of the theory already worked out for bromine (J., 1937, 1681) yields the equation

$$RK\Delta p = 2I_{abs.} - Y \qquad \qquad (1)$$

where

$$Y = \frac{S\{\sqrt{S^2 + 8I_{abs.}([Cl_2]k_{Cl_2} + [M]k_M)} - S\}}{2([Cl_2]k_{Cl_2} + [M]k_M)}$$

Here Δp is the observed Budde effect, on absorption of light $I_{abs.}$, K being the thermal conductivity of the gas mixture, R is a constant, k_{Cl_2} and k_M triple collision coefficients, and S the factor measuring the diffusion of atoms to the wall. This formula may be tested at once by reference to the variation of $I_{abs.}$. For a given gas mixture all other factors remain constant; if the above mechanism is the correct one, the observed Δp will not be directly proportional to $I_{abs.}$

The sensitivity of the photronic cell varied with the wave-length and therefore filter solutions or glass plates could not be conveniently employed to alter the intensity. The rotating-sector method was accordingly adopted to give a reduced intensity of approximately half the initial value; a greater reduction gave values of Δp too small for sufficiently accurate measurement. Results are in Table I.

TABLE I.

$[Cl_2]$ = 50·0 mm.

Ratio of intensities = 0·535.

	Pressure of added gas (mm.).	Δp (full).	Δp (reduced).	Ratio.		Pressure of added gas (mm.).	Δp (full).	Δp (reduced).	Ratio.
[A] =	0	1·0	0·5	0·50	[HCl] =	0	0·8	0·4	0·50
	100	2·0	1·0	0·50		100	1·7	0·9	0·53
	200	2·5	1·35	0·53		200	2·3	1·3	0·56
	300	3·3	1·7	0·515		300	3·3	1·8	0·545
	500	4·3	2·2	0·51		400	4·0	2·1	0·525
						500	4·5	2·4	0·53

Within the limits of experimental error ($\pm$ 0·1 div.), Δp is proportional to $I_{abs.}$ over the entire range. Further examination of (1) in relation to Δp for given conditions (see Table II) shows that even for nitrogen and argon, where a constant relative triple collision efficiency is indicated (cf. Ritchie, J., 1937, 863) and where gas addition offers the minimum disturbance from the point of view of altered wall film, such a formula cannot be made to cover the experimental results. If, for example, constants are chosen to fit one portion of the nitrogen curve of Δp plotted against $[N_2]$, the remainder of the curve shows ever-increasing divergence, and examination of the corresponding argon series, theoretically calculable from the nitrogen curve, leads to similar conclusions. It is therefore deduced that under the given conditions recombination of chlorine atoms does not take place by a process analogous to the recombination processes of bromine and iodine atoms.

Mechanism 2.

(i) $Cl_2 \xrightarrow{h\nu} Cl + Cl$ .... k_1 (iv) $Cl \longrightarrow \frac{1}{2}Cl_2$ at surface ... S
(ii) $Cl + Cl_2 \longrightarrow Cl_3$ .... k_2 (v) $Cl_3 \longrightarrow \frac{3}{2}Cl_2$ at surface ... S'
(iii) $Cl_3 + Cl_3 \longrightarrow 3Cl_2$ .... k_3

The rise in pressure on illumination will be due to the heat liberated in reactions (ii) and (iii). Adsorption of chlorine atoms and Cl_3 molecules on the wall will reduce the heat effect, and hence diffusion of both species to the walls should be considered. It does not follow that such adsorption will occur at every collision with the wall; and Craggs, Squire, and Allmand (J., 1937 1886) have indicated that different surfaces may have different efficiences of adsorption of Cl and Cl_3. The Cl_3 molecule by virtue of its size and weight will diffuse much more slowly; the difficulties of calculation of effective diffusion for both Cl and Cl_3 are such that the assumption has here been made that the adsorption of Cl_3 is inappreciable. This, of course, will not be exactly correct, as indicated by the " adsorption effect " above mentioned, but in view of the smallness of the effect, the broad conclusions drawn are regarded as justifiable.

If all Cl_3 molecules formed are then converted into Cl_2 molecules, the heat produced in the gas phase per second is proportional to $[Cl][Cl_2]$, and in the steady state, will be equal to the heat transferred to the walls per second. The rise in temperature will depend on the thermal conductivity of the gas mixture. In the present experiments, with a relatively narrow light beam fixed in position, we may apply the general conductivity formula $Q = KA\Delta T/x$ in the form $Q \propto K\Delta T$, where Q is the heat transferred per second to the walls, K is the thermal conductivity of the gas, and ΔT the rise in temperature in the steady state. For any gas mixture, the increase in pressure is proportional to the rise in temperature: hence $Q \propto K\Delta p$, and $K\Delta p \propto [Cl][Cl_2]$. In the photostationary state, by mechanism 2, $d[Cl]/dt = k_1 I_{abs.} - k_2[Cl][Cl_2] - S[Cl] = 0$ where S is the factor representing the rate of diffusion of chlorine atoms to the wall. Hence $[Cl] = k_1 I_{abs.}/(S + k_2[Cl_2])$ and

$$K\Delta p \propto [Cl_2]k_1 I_{abs.}/(S + k_2[Cl_2]) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This expression meets the requirement that $\Delta p \propto I_{abs.}$; it may be further noted that if an appreciable number of Cl_3 molecules should be adsorbed at the wall, the competition between this process and the bimolecular recombination to form Cl_2 molecules would yield an $I_{abs.}^{\frac{1}{2}}$ term in the expression for Δp contrary to experiment.

The testing of (2) with regard to variation of $[Cl_2]$ cannot be conveniently examined, because increase of chlorine pressure, say, causes the position of maximum absorption to move nearer to the wall where the light enters, thus altering the position of the source of chlorine atoms and increasing the difficulty of calculation of the diffusion factors for the various pressures. It can, however, be tested in relation to S by the addition of other gases.

If t is the time taken for a chlorine atom to diffuse a given distance through chlorine gas, $t \propto 1/D_{Cl_2}$, where D_{Cl_2}, the diffusion factor, is given by $(1/M_A + 1/M_M)^{\frac{1}{2}}/[M]\sigma^2_{AM}$. Here M_A is the weight of the diffusing atom, M_M the molecular weight of the gas through which the atom diffuses, [M] the pressure of such gas, and σ_{AM} the sum of the radii of diffusing particle and gas molecule. For a mixture of two gases, we take $t \propto (1/D_1 + 1/D_2)$, and since $S \propto 1/t$, $S = m(1/D_1 + 1/D_2)^{-1}$, where m is a constant depending on the vessel dimensions, etc.

Use was made of the following constants: $\sigma_{Cl_2} = 3{\cdot}6 \times 10^{-8}$ cm., $\sigma_{N_2} = 3{\cdot}1 \times 10^{-8}$ cm.,

$\sigma_{O_2} = 2{\cdot}9 \times 10^{-8}$ cm., $\sigma_A = 2{\cdot}86 \times 10^{-8}$ cm., $\sigma_{HCl} = 3{\cdot}0 \times 10^{-8}$ cm., $\sigma_{CO_2} = 3{\cdot}8 \times 10^{-8}$ cm.; σ_{Cl} was taken as $2{\cdot}0 \times 10^{-8}$ c.m.

Thermal Conductivities.—As concordant values of the thermal conductivity of hydrogen chloride were not obtainable, direct measurements of relative values for the various gases and gas mixtures were carried out. Use was made of the hot-wire method, where a thin platinum wire (7 cm. long and of 0·0076 cm. diameter) was supported, approximately in the position occupied by the light beam, in the reaction vessel, and its temperature raised electrically by a current at constant voltage. The heat produced gave an increase in pressure of approximately the same magnitude as the Budde effects themselves. The resistance of the wire was then determined in the usual way for the various gases and gas mixtures. Contrary to expectation, the resistance of the wire did not remain at a constant value for different pressures of added single gases but decreased regularly as the pressure was increased. By taking the resistances at single gas pressures of 50 mm. as standard, however, it was found that the same correction for all gases at the same pressures restored the compensating resistances (proportional to the resistance of the wire) to the standard values at 50 mm., thus :

Gas.	R_{50} (ohms).	R_{350} (ohms).	Correction.	Gas.	R_{50} (ohms).	R_{350} (ohms).	Correction.
N_2	2246	2147	99	O_2	2232	2133	99
CO_2	2506	2410	96	HCl	2435	2337	98

Convection was considered to be the cause of the divergences from the expected constant values. Since the correction was applicable to single gases, it was considered applicable to mixtures of chlorine with these gases; when this was done, the values of thermal conductivity of the mixtures were almost exactly those calculated from the single gas conductivity values by the formula assuming conductivities to be linear functions of the composition :

$$K = \left[\frac{(K_M - K_{Cl_2})[M]}{([Cl_2] + [M])}\right] + K_{Cl_2}$$

Such values of K are given in Table II : values for single gases are

$$K_{Cl_2} = 0{\cdot}72,\ K_{N_2} = 2{\cdot}28,\ K_{O_2} = 2{\cdot}33,\ K_A = 1{\cdot}58,\ K_{HCl} = 1{\cdot}61,\ K_{CO_2} = 1{\cdot}37.$$

It was found that $I_{abs.}$ remained constant and independent of the added gas; equation (2) may then be put in the form

$$RK\Delta p = [Cl_2]/(S + [Cl_2]) = 1/(mD/[Cl_2] + 1)$$

where R is a constant and $D = (1/D_{Cl_2} + 1/D_M)^{-1}$.

If we now apply this expression to any two results in the nitrogen series, say $[N_2] = 0$ and $[N_2] = 300$ mm., with appropriate values of D (see Table II), we find that m has apparently negative values, similar results being obtained in the argon series. It is therefore concluded that mechanism 2 does not represent the recombination process.

If we consider equation (ii) as reversible by introducing $Cl_3 \longrightarrow Cl_2 + Cl$, with coefficient k_4, the heat produced in the gas phase then involves the three terms : $k_2[Cl][Cl_2]$, $k_4[Cl_3]$, and $k_3[Cl_3]^2$. Since as much heat must be absorbed in the reverse action as is liberated in the forward action (ii),

$$Q = k_2'(k_2[Cl][Cl_2] - k_4[Cl_3]) + k_3'k_3[Cl_3]^2$$

where k_2' and k_3' take account of the fact that different amounts of heat are involved in the two stages. For equilibrium conditions represented by the reversible equation $Cl + Cl_2 \rightleftharpoons Cl_3$, the equilibrium constant $k = [Cl][Cl_2]/[Cl_3]$, and application of the previous method gives $Q \propto I_{abs.}[Cl_2]/[S + (k_2 - k_3/k)[Cl_2])$, which is of the same general type as before. No distinction thus appears between the two mechanisms. If the Cl_3 equilibrium is not attained, the analysis is more complicated and yields terms in $I_{abs.}^{\frac{1}{2}}$. It is thus concluded that the mechanisms so far examined are not in accordance with experiment.

Mechanism 3.

(i) $Cl_2 \xrightarrow{h\nu} Cl + Cl$ .... k_1

(ii) $Cl + Cl_2 + M \longrightarrow Cl_3 + M$ ... k_2

(iii) $Cl_3 + Cl_3 \longrightarrow 3Cl_2$ ...... k_3

(iv) $Cl \longrightarrow \frac{1}{2}Cl_2$ at surface ...... S

In this case the heat produced in the gas phase is proportional to $[\mathrm{Cl}][\mathrm{Cl}_2][\mathrm{M}]$. Since

$$d[\mathrm{Cl}]/dt = k_1 I_{\mathrm{abs.}} - k_2[\mathrm{Cl}][\mathrm{Cl}_2][\mathrm{M}] - S[\mathrm{Cl}] = 0$$

$$[\mathrm{Cl}] = k_1 I_{\mathrm{abs.}}/(k_2[\mathrm{Cl}_2][\mathrm{M}] + S)$$

and

$$K\Delta p \propto k_1 I_{\mathrm{abs.}}[\mathrm{M}][\mathrm{Cl}_2]/(k_2[\mathrm{Cl}_2][\mathrm{M}] + S) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here M may be either of the gases of the mixture, and since each gas must be taken to have a different triple collision coefficient, the final expression for a binary mixture, $I_{\mathrm{abs.}}$ being constant, is

$$RK\Delta p = [\mathrm{Cl}_2]([\mathrm{Cl}_2] + k_{\mathrm{M}}[\mathrm{M}])/[[\mathrm{Cl}_2]([\mathrm{Cl}_2] + k_{\mathrm{M}}[\mathrm{M}]) + mD] \quad . \quad . \quad . \quad (4)$$

where k_{M} is the triple collision coefficient of the added gas referred to the chlorine coefficient as unity. Putting $([\mathrm{Cl}_2] + k_{\mathrm{M}}[\mathrm{M}]) = Y$, and $z = mD/[\mathrm{Cl}_2]Y$, we have

$$\Delta p = 1/[RK(1 + z)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Results for the various gas mixtures are in Table II.

TABLE II.

$[\mathrm{Cl}_2] = 50{\cdot}0$ mm.

Press. of added gas, mm.	$D \times 10^{-12}$.	$mD/50$.	Y.	z.	$1 + z$.	K.	Δp (calc.).	Δp (obs.).	Δp (calc.)/Δp (obs.)
Nitrogen : $m = 0{\cdot}48 \times 10^{-8}$, $k_{\mathrm{N}_2} = 0{\cdot}49$, $R = 0{\cdot}050$.									
0	5·26	505	50	10·1	11·1	0·72	2·50	2·5	1·00
100	2·24	215	99	2·17	3·17	1·65	3·92	3·9	1·01
200	1·42	131	148	0·88	1·88	1·97	5·40	5·2	1·04
300	1·04	100	197	0·51	1·51	2·06	6·42	6·4	1·00
400	0·82	79	246	0·32	1·32	2·10	7·21	7·2	1·00
500	0·68	65	295	0·22	1·22	2·14	7·66	7·6	1·01
600	0·58	56	344	0·16	1·16	2·16	7·98	7·9	1·01
Argon : $m = 0{\cdot}58 \times 10^{-8}$, $k_{\mathrm{A}} = 0{\cdot}26$, $R = 0{\cdot}042$.									
0	5·26	610	50	12·2	13·2	0·72	2·51	2·5	1·00
100	2·38	276	76	3·63	4·63	1·15	4·47	4·8	0·93
200	1·53	177	102	1·73	2·73	1·41	6·20	6·3	0·98
300	1·12	130	128	1·015	2·01	1·46	8·07	8·0	1·01
400	0·90	104	154	0·675	1·67	1·49	9·55	9·6	0·99
500	0·74	86	180	0·48	1·48	1·50	10·7	10·7	1·00
600	0·63	73	206	0·35	1·35	1·52	11·6	11·6	1·00
Oxygen : $m = 0{\cdot}54 \times 10^{-8}$, $k_{\mathrm{O}_2} = 0{\cdot}54$, $R = 0{\cdot}045$.									
0	5·26	568	50	11·35	12·35	0·72	2·50	2·5	1·00
100	2·29	247	104	2·37	3·37	1·79	3·68	3·7	1·00
200	1·32	143	158	0·905	1·905	2·01	5·80	5·3	1·09
300	1·08	117	212	0·55	1·55	2·10	6·82	6·8	1·00
400	0·85	92	266	0·35	1·35	2·15	7·64	7·1	1·07
500	0·70	75·6	320	0·24	1·24	2·18	8·20	8·0	1·02
600	0·59	63·7	374	0·17	1·17	2·21	8·60	8·6	1·00
Hydrogen chloride : $m = 0{\cdot}83 \times 10^{-8}$, $k_{\mathrm{HCl}} = 0{\cdot}26$, $R = 0{\cdot}030$.									
0	5·26	873	50	17·4	18·4	0·72	2·50	2·5	1·00
100	2·19	364	76	4·79	5·79	1·30	4·40	4·4	1·00
200	1·38	229	102	2·24	3·24	1·42	7·19	7·2	1·00
300	1·01	168	128	1·31	2·31	1·47	9·75	9·9	0·98
400	0·74	123	154	0·80	1·80	1·50	12·2	12·1	1·01
500	0·66	109	180	0·61	1·61	1·52	13·5	13·7	0·99
600	0·555	92	206	0·45	1·45	1·53	14·9	15·1	0·99
Carbon dioxide : $m = 0{\cdot}455 \times 10^{-8}$, $k_{\mathrm{CO}_2} = 0{\cdot}13$, $R = 0{\cdot}0518$.									
0	5·26	479	50	9·58	10·58	0·72	2·54	2·5	1·02
100	2·02	184	63	2·92	3·92	1·15	4·29	4·5	0·95
200	1·25	114	76	1·50	2·50	1·24	6·23	6·2	1·00
300	0·90	82·4	89	0·925	1·93	1·28	7·85	7·7	1·02
400	0·76	69·5	102	0·69	1·69	1·30	8·80	9·0	0·98
500	0·58	53·1	115	0·46	1·46	1·31	10·1	10·1	1·00
600	0·495	45·0	128	0·35	1·35	1·32	10·9	11·2	0·97

It will be observed that (5) leads to values in good agreement with experimental results. The values of the constants m and R are sensibly the same for all the gases except hydrogen chloride, for which m is somewhat greater and R less. The constant m expresses the rate at which atoms reach the wall and are removed; the high value for hydrogen chloride would therefore indicate a greater efficiency of adsorption of chlorine atoms by a surface carrying adsorbed hydrogen chloride, in agreement with previous conclusions.

Craggs and Allmand (J., 1937, 1889) found that the addition of water vapour slightly decreased the rate of photosynthesis of hydrogen chloride under conditions where surface action was appreciable; a surface carrying adsorbed water was considered slightly more efficient in removing chain carriers. The addition of 2 mm. of water vapour to 50 mm. of chlorine showed a Budde effect slightly less than the value obtained with dry gas (2·3 and 2·5 respectively). The value of 2·5 was also obtained when the vessel had been previously " baked-out " at 300—350°. These results thus confirm Craggs and Allmand's conclusions. At higher pressures of added gas, approximately the same values of Δp were obtained for both wet and dry mixtures, as expected.

In considering relative values of k as used in the above table, it is to be remembered that such values represent relative triple collision velocity coefficients only when the stabilisation of Cl_3 is concerned; if any other reaction occurs, k would give relative values of the product of heat of reaction and velocity coefficient. For chlorine, nitrogen, and argon, where the Cl_3 stabilisation is the only probable process, the relative k values are 2·03, 1·00, and 0·53 respectively. The $k_{N_2} : k_A$ ratio compares very favourably with ratios determined in other stabilisations (O_3, Br_2, I_2, HO_2); the value for oxygen (1·10) is similarly in agreement with the conclusion of Rabinovitch and Wood (*Trans. Faraday Soc.*, 1936, **32**, 907) that such efficiency is higher for diatomic than for monatomic molecules, and increases with growing molecular size and the intensity of the molecular fields of the colliding particles. The value for k_{HCl}/k_{N_2} (0·53) here obtained is considerably different from that recorded in the H–O_2 reaction (Ritchie, J., 1937, 863) where $k_{HCl}/k_{N_2} = 5{\cdot}4$; it would appear that the present value is more consistent with size and molecular weight than the higher figure, obtained for a triple collision which may not result in the stabilisation of HO_2, but may give as products H_2O and ClO.

The ratio $k_{CO_2} : k_{N_2} = 0{\cdot}27$ is much less than the ratios obtained in other stabilisations (1·4—2·7), and it is difficult to visualise other suitable reactions which might occur on collision of Cl, Cl_2, and CO_2. In the examination of the Budde effect in bromine, carbon dioxide was abnormal in that no constant values of m and R could be found to fit experimental results over the entire pressure range, a progressive change in surface conditions being regarded as responsible; it is possible that the small value of 0·27 may not be unconnected with similar phenomena. It may also be of importance in this connection that the " adsorption effect " earlier discussed was not observed for chlorine–carbon dioxide and –hydrogen chloride mixtures, and this may again be taken to indicate a difference in surface conditions in these gases when compared with the more permanent gases nitrogen, argon, and oxygen.

It should be pointed out that if equation (ii) of mechanism 3 is reversible and equilibrium is established, the heat then produced in the gas phase can be expressed by an equation of the form

$$Q \propto [Cl_2]k_1 I_{abs.}/(S + k'[Cl_2][M])$$

which is of the same general type as before. Present calculations therefore do not admit of distinction being made between these two mechanisms.

It thus appears probable that in any reaction involving chlorine where the recombination of chlorine atoms is of importance, added inert gas or products of reaction will tend to reduce the concentration of chlorine atoms by means of the triple-collision process $Cl + Cl_2 + M \longrightarrow Cl_3 + M$. The rate of photocombination of hydrogen and chlorine should therefore be retarded under certain conditions by the product, hydrogen chloride. The retardation recorded for this reaction by Ritchie and Norrish (*loc. cit.*) is much greater than is to be expected from the above coefficients; but as their rates of reaction were not exactly proportional to $I_{abs.}^{\frac{1}{2}}$, surface action was apparently considerable, and this may be connected with the divergence.

In this connection some preliminary results on this photosynthesis, carried out by the method employed by Ritchie and Norrish, are given. A high-intensity source of light was used, the time of reaction being reduced for comparable concentrations of reactants by a factor of ten, to obtain a rate proportional to $I_{\text{abs.}}^{\frac{1}{2}}$; the results in this respect were disappointing, the index being of the order 0·85, and surface action apparently present. For changes in hydrogen chloride pressure which are not too large, however, such surface effects may be considered as remaining constant; retardation of the rate of H_2–Cl_2 combination may then be kinetically derived, on the basis of the above triple collision, by the factor $1/([Cl_2] + k[HCl])$, where k is the relative collision efficiency of hydrogen chloride to chlorine. For $[H_2] = [Cl_2] = 43$ mm., the quantum efficiency of hydrogen chloride formation was found experimentally to be 8350 at $[HCl] = 15$ mm. and 5800 at $[HCl] = 115$ mm. The hydrogen chloride was prepared by illumination in the silica reaction vessel itself, and the retardation was not therefore due to any accidentally introduced inhibitors; Draper effects were always sharp and immediate. The value of k calculated from these results is 0·21, in fair agreement with the value of 0·26 derived from the Budde measurements.

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