ON THE PHOTOCHEMICAL UNION OF HYDROGEN AND CHLORINE.*

By MIKIO TAMURA.

Most of all the preceding works on the photochemical union of hydrogen and chlorine only deal with the reaction in photostationary state. For the elucidation of the reaction mechanism it is necessary, of course, to study the reaction velocities before the photostationary state is established as well as those after shutting off light. To trace the change of these reaction velocities with time, the method of thermal analysis, which originated with Prof. S. Horiba, was used. The author already studied the photochemical formation of phosgene[1] by this method and evaluated the mean life of chain, the concentration of chain carriers and the collision yields of some partial reactions from the experimental results, applying the theory of chain reactions; and these measurements have been extended here to the photochemical formation of hydrogen chloride.

Experimental Method.

Here will be given only an outline of the experimental method, as it is the same as that of the studies on the photochemical formation of hydrogen chloride by Prof. S. Horiba and Dr. T. Ichikawa[2] and on the photochemical formation of phosgene by the present author.[1]

The increase of the pressure of a gas mixture due to the heat of reaction is recorded on a photographic film, and from the record the reaction velocity $\frac{dx}{dt}$ is calculated by the following equation:[1,2]

$$K\frac{dx}{dt}=\frac{d(\varDelta p)}{dt}+k(\varDelta p), \qquad (1)$$

where K and k are constants, the values of which can be easily obtained, and $\varDelta p$ is the increase of pressure.

Equation (1) was derived from the following considerations. Assuming that the mixture of the reacting gases is subject to the ideal gas law, the state of the gas mixture at a given instant will be given in the following equation.

$$p_1V=nRT_1, \qquad (a)$$

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* This paper is the English translation of the same article which appeared in this journal, 8, 59, 1936.

[1] M. Tamura, *Rev. Phys. Chem. Japan*, 7, 49 (1933).

[2] S. Horiba and T. Ichikawa, *Rev. Phys. Chem. Japan*, 1, 145 (1927), "Sexagint" (a collection of papers dedicated to Prof. Y. Osaka) 73 (1927). T. Ichikawa, *Rev. Phys. Chem. Japan*, 4, 1 (1930); *Z. physik. Chem.* (*B*). 10, 299 (1930).

where V is the volume of the reaction vessel, and p_1, n and T_1 are the pressure, the number of mols and the temperature of gas mixture in the reaction vessel at a given instant respectively. Differentiating equation (a) with regard to time, we have

$$\frac{dp_1}{dt}=\frac{nR}{V}\,\frac{dT_1}{dt}. \tag{b}$$

The initial temperature (room temperature) being denoted by T, the initial pressure in the reaction vessel by p; and if we put $p_1=p+\Delta p$, $T_1=T+\Delta T$; from equation (b) we have

$$\frac{d(\Delta p)}{dt}=\frac{nR}{V}\,\frac{d(\Delta T)}{dt}. \tag{c}$$

Let us suppose that dx mols of hydrogen chloride is formed during the time interval dt, then the increase in the temperature of this system will be expressed as follows:

$$dT_1=\frac{Q\,dx}{s\delta V}, \tag{d}$$

where Q is the heat of formation of one mol of hydrogen chloride, and δ and s denote the specific gravity and the specific heat of the gas mixture respectively. But cooling occurs simultaneously with the evolution of the reaction heat, so that the real increase in the temperature of the system during the reaction would be expressed by

$$dT_1-dT_1'=\frac{Q\,dx}{s\delta V}-dT_1', \tag{e}$$

where $-dT_1'$ expresses the cooling effect. As for the cooling velocity, $-\frac{dT_1'}{dt}$, it must be a function of the difference between the temperatures of the reaction vessel and the surroundings, that is,

$$-\frac{dT_1'}{dt}=-f(T_1-T)=-f(\Delta T). \tag{f}$$

From equation (e) and (f) we have

$$dT_1-dT_1'=\frac{Q\,dx}{s\delta V}-f(\Delta T)\,dt.$$

Again, substituting dT_1-dT_1', the practical increase in temperature, for $d(\Delta T)$ in equation (c), we have

$$\frac{d(\Delta p)}{dt}=\frac{nR}{V}\,\frac{d(\Delta T)}{dt}=\frac{nRQ}{s\delta V^2}\,\frac{dx}{dt}-\frac{nR}{V}f(\Delta T). \tag{g}$$

$\frac{d(\Delta p)}{dt}$ can be found directly from the record on the film, and $\frac{nRQ}{s\delta V^2}$ may be regarded as constant during some short intervals of time, because the amount of the produced hydrogen chloride is very small against the total volume of the reacting gas, so that the change of s and δ is negligible. Now if we can determine the function $f(\Delta T)$, we shall be able to calculate the true reaction velocity, $\frac{dx}{dt}$, of our photochemical reaction. The simple law of heat conductivity $f(\Delta T)=k\Delta T$ being assumed, and the relation $\Delta T=\frac{V}{nR}\Delta p$ used, equation (g) will be written as follows:

$$\frac{d(\Delta p)}{dt}=\frac{nRQ}{s\delta V^2}\,\frac{dx}{dt}-k(\Delta p).$$

Putting $\frac{nRQ}{8\delta V^2} \equiv K$, here we get equation (1):

$$K\frac{dx}{dt} = \frac{d(\Delta p)}{dt} + k(\Delta p).$$

The value of k can be easily obtained from the curve recorded on the film after shutting off light.[1),2)]

We can thus calculate the reaction velocity at any time during the period of illumination and after shutting off light.

Preparation of Reactants.

Chlorine was prepared by electrolysing a solution of potassium chloride acidified with hydrochloric acid. The gas was purified by washing with water and then with sulphuric acid both in darkened vessels, and was passed through a tube filled with glass balls, and heated at 350°C., and then was collected by means of solid carbon dioxide. This "crude" chlorine was then subjected to repeated fractional distillation. The distillation was repeated three times, the receiving bulb being cooled in liquid air, and the distilling bulb in solid carbon dioxide; in each distillation the initial quarter of the distillate and the final quarter were rejected. To expel impure gases, the vessel was evacuated in each distillation up to ca. 10^{-4}mm.Hg by means of Volmer's pump, chlorine being kept in solid state by liquid air. Much care was taken as to the exculsion of oxygen, the air in the generator being previously replaced as thoroughly as possible with chlorine, and the reservoir being also evacuated beforehand.

Hydrogen was obtained from the commercial bomb of electrolytically prepared hydrogen. The gas was washed with sulphuric acid, and passed over platinum asbestos heated at 300°C and then dried by means of solid carbon dioxide. The reservoir was washed several times with the pure hydrogen thus obtained.

Experiments.

The reaction vessel was washed several times with chlorine, and the grease used was that treated with chlorine and heated in vacuum. The pressures of reacting gases were read by a mercury manometer, a spring manometer of Pyrex glass being used as the zero point instrument to avoid the direct contact of mercury with chlorine.

The sensitivity of the gas mixture to light, after its introduction to the reaction vessel, decreased gradually even in the dark (in the course of 2 or 3 hours) until a certain constant value (about 80% of the initial value) was attained.[3)] The gas mixture was further illuminated five times, for 20 seconds at a time, in order to destroy any inhibiting impurities; but this precaution was unnecessary, since

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3) This decrease in the sensitivity may be probably due to some impurities from the grease and the cement used, notwithstanding our previous treatment of them with chlorine.

no change in the sensitvity was shown by this procedure and the observed reaction velocity was reproducible. This proved that there is no induction period in this reaction.

A) Change of the Reaction Velocity during Exposure.

Effect of Light Intensity and Quantum Yield.

One of the records is shown in Table I. The reaction velocities calculated from these records are given in Table II and Fig. 1. Expts. I, II and III were carried out under the same conditions and Expts. IV and V with weaker light intensity than in the former cases and Expts. VI and VII with still far weaker one. The stationary state, as is seen in Fig. 1, is reached within 0.2 sec. after the projection of light in every case.

Table I.

Expt. III. $(Cl_2)=258$mm. $(H_2)=100$mm. $(HCl)=7$mm. 21°C.

Light source: a 1000 C. P. Pointolite lamp, operating from a battery supply. The light was passed through a 78mm. layer of a solution $\left(\frac{CuSO_4+1080NH_3}{90}\ \text{(normal)}.\right)$.

Time $\left(\frac{1}{5}\text{ sec.}\right)$	Δp (mm.)	Time $\left(\frac{1}{5}\text{ sec.}\right)$	Δp (mm.)	Time $\left(\frac{1}{5}\text{ sec.}\right)$	Δp (mm).
Light on 0	0	7.5	0.64	Light off 23.1	0.92
0.2	0.03	8.0	0.58	23.2	0.92
0.5	0.07	8.5	0.52	23.3	0.90
1.0	0.19	9.0	0.48	23.4	0.88
2.0	0.35	10.0	0.40	23.5	0.86
3.0	0.48	11.0	0.34	23.6	0.84
4.0	0.58	12.0	0.26	23.7	0.83
5.0	0.67	13.0	0.22	23.8	0.81
6.0	0.75	14.0	0.20	23.9	0.78
Light off 6.3	0.76	15.0	0.17	24.0	0.79
6.4	0.76	Light on 15.1	0.17	24.5	0.72
6.5	0.75	15.5	0.23	25.0	0.66
6.6	0.75	16.0	0.32	25.5	0.63
6.7	0.73	17.0	0.45	26.0	0.55
6.8	0.71	18.0	0.58	27.0	0.43
6.9	0.70	19.0	0.67	28.0	0.38
7.0	0.69	20.0	0.75	29.0	0.32
7.1	0.67	21.0	0.80	30.0	0.26
7.2	0.65	22.0	0.87	31.0	0.22
7.3	0.65	23.0	0.92	32.0	0.19

Table II.

Change of the reaction veloctiy during the exposure.

21°C. $(Cl_2)=258$mm. $(H_2)=100$mm. $(HCl)=7$mm.

Expt. no.	I	II	III		IV	V	VI	VII
			1st exposure	2nd exposure				
Light intensity in arbitrary unit	1	1	1	1	0.42	0.42	0.13	0.13
Time (sec.)	$\frac{dx}{dt}\cdot 10^7$ mol/sec.	$\frac{dx}{dt}\cdot 10^7$ mol/sec.	$\frac{dx}{dt}\cdot 10^7$ mol/sec.	$\frac{dx}{dt}\cdot 10^7$ mol/sec.	$\frac{dx}{dt}\cdot 10_7$ mol/sec.	$\frac{dx}{dt}\cdot 10^7$ mol/sec.	$\frac{dx}{dt}\cdot 10^7$ mol/sec.	$\frac{dx}{dt}\cdot 10^7$ mol/sec.
Light on 0	—	—	—	—	—	—	—	—
0.1	7.35	7.29	7.39	7.04	4.03	4.20	1.92	1.89
0.2	7.56	7.46	7.46	7.56	4.16	4.16	2.28	2.28
0.4	7.39	7.35	7.25	7.32	4.13	4.16	2.31	2.31
0.6	7.18	6.93	7.11	7.25	4.20	4.16	2.24	2.38
0.8	6.97	6.93	6.97	7.07	4.27	4.24	2.34	2.31
1.0	7.07	7.00	7.11	7.18	4.24	4.20	2.24	2.14
1.2	7.14	7.04	7.04	7.11	4.31	4.24	2.14	2.17
1.4	7.25	7.04	—	7.25	4.24	4.24	2.17	2.17
1.6	7.28	—	—	—	4.27	4.34	2.17	2.17
1.8	7.14	—	—	—	4.34	4.34	2.20	2.20
2.0	7.00	—	—	—	—	4.34	2.24	2.20
2.2	6.97	—	—	—	—	4.31	—	—

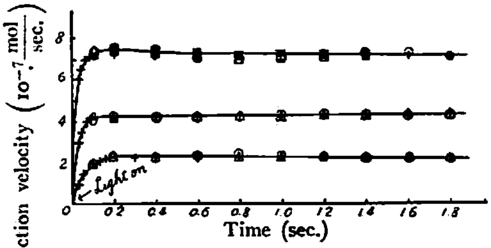

Fig. 1.

From the above experimental data, we notice that the reaction velocity in the stationary state is nearly proportional to a fractional power of the light intensity, namely,

$$\frac{dx}{dt}=kI_0^{0.6}.$$

The values of *k* calculated from the results of the experiments are given in the fourth column of Table III; the constancy is fairly satisfactory.

Table III.

Expt. no.	Light intensity in arbitrary unit	Reaction velocity in stationary state (10^{-7}mol/sec.)	*k*	Quantum yield
I II III	1.00	7.14	7.1	1760
IV V	0.42	4.29	7.2	2490
VI VII	0.13	2.19	7.5	4130

According to Bodenstein and Unger[4], and Kornfeld and Müller[5] the reaction velocity is directly proportional to the light intensity, but the results of Chapman and Gibbs[6] indicate that the reaction velocity is proportional to a power, less than unity, of absorbed light, and Ritchie and Norrish[7] obtained the same result as the present author's. The power, of course, depends not only upon the purity and the pressure of the gas and the volume of the reaction vessel, but also upon the light intensity. And indeed, the power may approach to unity in very weak light intensity and to 0.5 in moderate light intensity, and may again become large and even greater than unity[8] in very strong light intensity.

As shown in Table III, the quantum yields were also measured, the wave length of the light used being in the neighbourhood of 4400Å.

Table IV.

Change of the reaction velocity after shutting off light.

Expt. no.	I	II	III	
			1st Rec.	2nd Rec.
Time (sec.)	$\frac{dx}{dt}\cdot 10^7$ mol/sec.	$\frac{dx}{dt}\cdot 10^7$ mol/sec.	$\frac{dx}{dt}\cdot 10^7$ mol/sec.	$\frac{dx}{dt}\cdot 10^7$ mol/sec.
Light off 0	7.14	7.14	7.14	7.14
0.1	1.05	1.19	0.88	0.88
0.2	0.25	0.18	0.39	0.49
0.3	0.14	0.04	0.11	0.28

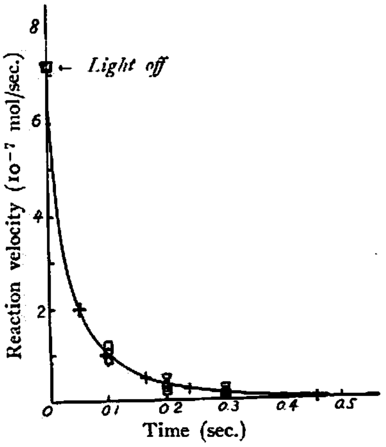

Fig. 2.

B) Reaction Velocity after Shutting off Light.

After shutting off light, the reaction velocity does not immediately vanish, but it runs as shown in Table IV. From these results, we can plot the most probable velocity curve as shown in Fig. 2 (Crosses indicate the calculated values, which will be explained later.).

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4) Bodenstein and Unger, *Z. Physik Chem.* (*B*) **11**, 253 (1931).
5) Kornfeld and Müller, *Z. physik Chem.*, **117**. 242 (1925).
6) Chapman and Gibbs, *Nature*, **127**, 854 (1931).
7) Ritchie and Norrish, *Proc. Roy. Soc.* (*A*), **140**, 99 (1933).
8) Kokotschaschwili, *Z. physik. Chem.*, (*B*), **23**, 431 (1933).

Discussion.

A) Collision Yield of the Partial Reaction, $Cl+H_2 \rightarrow HCl+H$.

Many kinds of the reaction mechanism have been proposed to account for the influence of water vapour since it was experimentally demonstrated by Coehn and Jung[9], and Coehn and Tramm[10]. But Rollefson[11], Rodebush and Klingerhöfer[12], Allmand and Craggs[13], and Bernreuther[14] could not observe such an effect of water vapour as Coehn and Jung stated. According to Kimball and Eyring[15], it seems impossible from the quantum mechanical considerations that water can help the combination of hydrogen and chlorine. We, therefore, use the Nernst chain for simplicity.

$Cl_2+h\nu=2Cl$ (1)

$Cl+H_2=HCl+H$ (2)

$H+Cl_2=HCl+Cl$ (3)

Some chain-breaking reactions. (4)[16]

The following considerations are not essentially affected by any modification in the Nernst chain so far as (2) and (3) are principal partial reactions. Except the case when light is very intense[5], the chain may not branch at room temperature.[17]

Now let the time taken for a chain link be τ sec., then two hydrogen chloride molecules are produced from one chlorine atom in τ sec. The life of chain are given by $T=\tau\nu$, ν being the length of the chain, or the number of chain links in a chain. The chain is indicated schematically in Fig. 3.

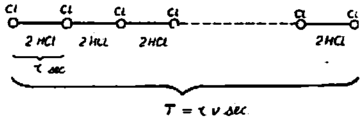

Fig. 3.

As τ is given by $\dfrac{\text{mean life of chain } (=T_m)}{\text{mean length of chain} (=\nu_m)}$ and the mean length of chain is a quarter of the quantum yield, we can evaluate τ from the experimental results in the following way.[1]

First T_m, the mean life of chain, is obtained from the velocity curve after shutting off light (e. g. from Fig. 2). Let V_0 represent the reaction velocity at the moment of shutting off light, then T_m is evidently given by

$$T_m=\frac{1}{V_0}\int_0^\infty V dt$$

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[9] Coehn and Jung, Z. *physik. Chem.*, **110**, 705 (1924)

[10] Coehn and Tramm, Z. *physik. Chem.*, **105**, 356 (1923).

[11] Rollefson, *J. Am. Chem. Soc.*, **55**, 860 (1933).

[12] Rodebush and Klingerhöfer, *J. Am. Chem. Soc.*, **55**, 130 (1933).

[13] Allmand and Craggs, *Nature*. **130**, 927 (1932).

[14] Bodenstein and Schenk, *Z. physik. Chem.* (B), **20**, 426 (1933).

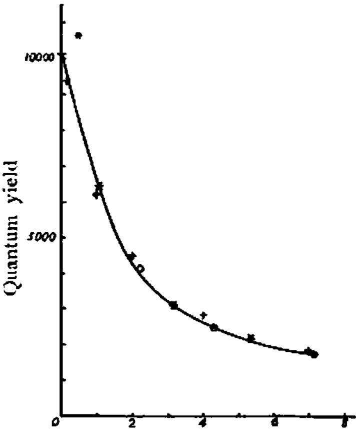
[15] Kimball and Eyring, *J. Am. Chem. Soc.* **54**, 3876 (1932).

[16] Whatever the partial reaction (4) may be, it never matters in our discussions.

[17] Kitagawa, *Rev. Phys. Chem. Japan*, **8**, 71 (1934).

and we have $T_m = \frac{1}{20}$ sec. from Fig. 2.

Secondly, the mean length of the chain ν_m must be evaluated. The experimental results show that the velocity is proportional to nearly 0.5th power (actually 0.6th power) of the light intensity. So it is possible to conclude that the reaction chains are terminated principally by self-neutralisation—i. e. by the combination of chain carriers between themselves—rather than by such an inhibitor as oxygen or silicon oxychloride postulated by Bodenstein and Unger[4]; for. in the latter case, the velocity would become proportional to the first power of the light intensity. The chain, therefore, becomes longer, as the concentration of chain carriers becomes smaller or the reaction velecity becomes smaller, for the reaction velocity is proportional to the concentration of chain carriers. The relation between the quantum yield[18] and the reaction velocity is shown in Fig. 4 obtained from Table III. The observed values are indicated by circles and the calculated values by stars.



Reaction velocity (10^{-7} mol/sec.)
Fig. 4.

· The values indicated by stars were obtained in the following way. Let V represent the reaction velocity; I_0 the intensity of light, then

$$V = k\, I_0^{0.6},$$

where k is constant. As in our experiment the absorbed light, $I_{abs.}$, is proportional to I_0, we have

$$V = k_1\, I_{abs.}^{0.6}, \tag{1}$$

where k_1 is constant. On the other hand

$$V = k_2\, \gamma\, I_{abs.}, \tag{2}$$

where γ is the quantum yield, and k_2 constant. Eliminating $I_{abs.}$ from equations (1) and (2), we have

$$V\{1 - k_2 k_1^{-\frac{5}{3}} \gamma V^{\frac{2}{3}}\} = 0.$$

Excepting the case where $V=0$, we have

$$V^{\frac{2}{3}} \gamma = k_2^{-1} k_1^{\frac{5}{3}} = k', \tag{3}$$

where k' is a constant, the value of which can be obtained from the experimental results. Stars in Fig. 4 were obtained from equation (3).

According to the equation, $\frac{dx}{dt} = V = k\, I_0^{0.6}$ or $V^{\frac{2}{3}}\gamma = k'$, the quantum yield should be infintely large if the reaction velocity becomes small. But, when the velocity

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[18] In this case the quantum yield is 4×(mean length of chain).

decreases, that is, when the concentration of chain carriers becomes small, the effect of the wall of the reaction vessel[19] and of impurities can not be neglected, then the limiting value of the quantum yield may be considered as obtained by extrapolation in Fig. 4. Thus the mean quantum yield, accordingly the mean length of chain ν_m is easily obtained from Fig. 4 and is 950 in this case.

τ, therefore, is given by

$$\tau=\frac{T_m}{\nu_m}=\frac{1}{20}\times\frac{1}{950}sec.=\frac{1}{19000}\ sec.$$

τ is the time taken by a chain link, but the partial reaction (3) is far faster than the partial reaction (2) and the latter may be reasonably considered to require τ *sec.* The value of τ depends, of course, upon the partial pressures of component gases and temperature and may be considered as reciprocally proportional to the concentration of hydrogen.

Now let us evaluate the collision yield of the reaction (2). The number of collisions of a chlorine atom with hydrogen molecules in one second is given by

$$Z=2\ \sqrt{2\pi}\left(\frac{d_{Cl}+d_{H_2}}{2}\right)^2\sqrt{\frac{M_{Cl}+M_{H_2}}{M_{Cl}M_{H_2}}\cdot RT}\ N_{H_2},$$

where d is the diameter of the atom or the molecule, M the atomic weight or the molecular weight and N_{H_2} the number of hydrogen molecules contained in $1\,cm^3$. Assuming that the chlorine atom is spherical and has the same density as that of chlorine molecule, we have $d_{Cl}=2.6\times10^{-8}$ cm.[20] When the pressure of hydrogen is 1 atm. and the temperature 21°C, Z is 1.0×10^{10}. The collision yield of the partial reaction (2), therefore, is

$$\frac{1}{10^{10}\cdot\frac{100}{760}\cdot\frac{1}{19000}}=1.4\times10^{-5}.$$

This coincides with the values obtained by Rodebush and Klingerhöfer[12] in a different way, and does not differ so much from the one estimated by Bodenstein.[21]

B) Concentration of Chain Carriers.

Let n_0 represent the number of chlorine atoms produced by light in unit volume in one sec. and T_m the mean life of chain, then the product $n_0\,T_m$ represents the number of chain carriers in unit volume in the photostationary state.

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[19] Triffonoff, *Z. physik. Chem.*, (B) 3, 195 (1929).

[20] Loeb. "*Kinetic Theory of Gas*" p. 529 (1927).

[21] Bodenstein, *Trans. Farad. Soc.*, 27, 413 (1931).

The partial pressure of chain carriers, therefore, can be easily calculated. These values are given in Table V. Using the value of τ above obtained, the partial pressures of chain carriers in some experiments of other observers[22] were also calculated as shown in the last three rows in Table V.

Table V.

Expt. no.	n_0	T_m (sec.)	n_0T_m	Partial pressure of chain carriers (mm. Hg)	Number of " Dreierstoss "
I II III	$2.8 \cdot 10^{12}$	$\frac{1}{42}$	$6.6 \cdot 10^{10}$	$1.8 \cdot 10^{-6}$	0.0003
IV V	$1.2 \cdot 10^{12}$	$\frac{1}{30}$	$4.0 \cdot 10^{10}$	$1.1 \cdot 10^{-6}$	0.0002
VI VII	$0.36 \cdot 10^{12}$	$\frac{1}{19}$	$1.9 \cdot 10^{10}$	$0.53 \cdot ^{-6}$	0.0002
Ritchie and Norrish	$4.9 \cdot 10^{12}$	$\frac{1}{3.8}$	$1.3 \cdot 10^{12}$	$3.6 \cdot 10^{-5}$	0.015
Kornfeld and Müller	$5.5 \cdot 10^{14}$	$\frac{1}{12}$	$4.6 \cdot 10^{13}$	$1.3 \cdot 10^{-3}$	
	$5.5 \cdot 10^{14}$	1.0	$5.5 \cdot 10^{14}$	$1.5 \cdot 10^{-2}$	

As the collision yield for the partial reaction (3) may be of the order of 10^{-2}[21] and that for the partial reaction (2) $10^{-4} \sim 10^{-5}$, the concentration of chlorine atoms may be $100 \sim 1000$ times as large as that of hydrogen atoms and the partial pressure of chain carriers given in Table V may, therefore, be regarded as that of chlorine atoms. As seen from the Table, the concentration of chlorine atoms can take various values according to the experimental conditions.

The concentration of hydrogen atoms in this photochemical reaction was measured by Geib and Harteck[23] and evaluated to be 10^{-5} mm.Hg. This means that the concetration of chlorine atoms was $10^{-2} \sim 10^{-3}$ mm.Hg. This high value may be due to the great intensity of light used by them.

C) Mean Life of Chain.

T_m in Table V gives the mean life of chain in the photostationary state and these are $\frac{1}{20} \sim \frac{1}{40}$ sec. in the present experiments, which agree pretty well with the valuses $\frac{1}{20} \sim \frac{1}{100}$ sec. obtained by Weigert and Kellerman[24] by means of the

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[22] These experiments were made at room temperature as that of the author, so that when T_m was calculated, the influence of the partial pressure of hydrogen upon τ was taken into consideration, but not that of temperature.

[23] Geib and Harteck, *Z. physik. Chem.* (*B*), **15**, 116 (1931).

[24] Weigert and Kellerman, *Z. physik. Chem.* **107**, 1 (1923).

"Schlierenmethode". But as seen from Table V, the mean life, T_m, attains to 1 sec. under some experimental conditions.

D) Chain-breaking Reaction.

As already stated, from the fact that the reaction velocity is proportional to a fractional power of the absorbed light, it was concluded that the reaction chains are terminated principally by the combination of chain carriers between themselves, rather than by such an inhibitor as oxygen or any organic substance. But it is also evident that the triple collision, $Cl+Cl+M$ (third body)$\rightarrow Cl_2+M$, is not the principal reaction to break the chain, for by calculating the number of the triple collisions of the chlorine atoms belonging to a chain in its mean life T_m very small values are obtained in the present case as shown in the last column of Table V. The union of hydrogen atom and chlorine atom, as well as the recombination of hydrogen atoms by triple collision, may be less predominant than that of chlorine atoms. The union of these atoms on the surface of the reaction vessel may be also neglected.

Ritchie and Norrish[7] obtained the same relation between the reaction velocity and the light intensity as the present author did, but they did not observe the "third body effect", the absence of which may be also comprehended from the calculation of the number of triple collisions as shown in the last column of Table V.

The recombination of chlorine atoms may also occur according to the mechanism that a metastable $^2P_{1/2}$ and a normal $^2P_{3/2}$ chlorine atoms can recombine with light emission at the moment of collision without the intervention of a third body. But the collision yield may be of the order of 10^{-5} (transition probability of electron-energy to light-energy being 10^8 and the duration of collision 10^{-13} sec.[25]), and this recombination, therefore, is negligible in the present experiments.

Rollefson and Eyring[26] deduced from the quantum mechanical considerations that Cl_3 molecules should be formed from Cl atoms and Cl_2 molecules without the necessity of ternary collisions. If so, we must replace the Cl atoms in the Nernst chain by Cl_3 molecules, and the chain is considered to be terminated according to the reaction

$$2Cl_3 \rightarrow 3Cl_2,$$

to which triple collisions are unnecessary. To explain the dependence of reaction velocity on light intensity, the introduction of Cl_3 is convenient, but the existence and the predominance of Cl_3 at room temperature must be experimentally decided.

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[25] Bonhoeffer and Harteck, "*Grundlagen der Photochemie*" pp. 223–4 (1933).

[26] Rollefson and Eyring, *J. Am. Chem. Soc.* 54, 170 (1932).

E) Theoretical Curve.

There is no doubt that the chemical reaction between chlorine and hydrogen is a straight chain reaction in our experimental conditions—at room temperature, ordinary pressure, and in moderate light intensity. According to the experimental results, as the reaction velocity in a stationary state is of the fractional order (0.6) of light intensity, it is admitted that the chain breaks mainly due to the second order reaction with respect to the chain carrier. If the concentration of the chain carrier becomes small, the possibility of the chain-breaking due to the combination of one chain carrier with another will be small. On the contrary, the possibility of the very chain carrier combining with impurities or breaking on the wall is independent of the concentration of the chain carrier. Therefore, the chain chiefly breaks due to the first order reaction with respect to the chain carrier when the reaction velocity is small. From these considerations it is concluded that the decrease of the reaction velocity after shutting off light makes the break of chain so difficult that the rate of the decrease of the reaction velocity becomes small as shown in Table IV and Fig. 2. For example, the ratio of the velocity in 0.1 sec. to that at the very instant of shutting off light is $\frac{1.05}{7.14}=\frac{1}{6.8}$, while the ratio of the velocity in 0.2 sec. to that in 0.1 sec. is $\frac{0.25}{1.05}=\frac{1}{4.6}$.

It is needless to say that the curve in Fig. 4 should be explained by the relation between the reaction velocity and the degree of the chain-breaking. Now we will deduce the theoretical formulae of the curves in Figs. 1, 2 and 4 through the theory of chain reaction.

Let α be the probability that each chain link can lead to the formation of the next chain link; ν, the chain length; then

$$\nu=\frac{1}{-ln\,\alpha}.^{1),27)} \qquad (1)$$

If α is constant, the reaction velocity after shutting off light is represented by

$$V=V_0\,\alpha^{\frac{t}{\tau}}, \qquad (2)$$

where V is the reaction velocity, V_0 the one at the very instant when light is shut off. But, α, in the present case, is not a constant but a function of V and accordingly of time t, and the reaction velocity cannot be represented by such a simple equation as (2).

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27) If $\alpha \fallingdotseq 1$, $-ln\,\alpha$ is nearly equal to $1-\alpha$, whence $\nu=\frac{1}{-ln\,\alpha}\fallingdotseq\frac{1}{1-\alpha}$, which agrees with the expression obtained by Semenoff. See Semenoff, *Chem Rev.* 6, 347 (1929); Bursian and Sorokin, *Z. physik. Chem.*, (*B*) 12, 247 (1931).

Now let us consider how we can get the equation which can express exactly the experimental results. a can be regarded constant in a small interval of time; we, therefore, get from (2) the following relation

$$\left(\frac{dV}{dt}\right)_{t=0}=\left(V_0\frac{\ln a}{\tau}a^{\frac{t}{\tau}}\right)_{t=0}=\frac{V_0}{\tau}\ln a_0, \qquad (3)$$

where a_0 represents the probability at $t=0$. From (1) and (3) we have

$$\left(\frac{dV}{dt}\right)_{t=0}=-\frac{V_0}{\tau\nu_0}, \qquad (4)$$

where ν_0 is the chain length at $t=0$. Analogously we have the following relation at any time $t=t$.

$$\left(\frac{dV}{dt}\right)_{t=t}=-\frac{V_t}{\tau\nu_t}, \qquad (5)$$

where V_t and ν_t are the reaction velocity and chain length at $t=t$ respectively.

The reaction chains may be terminated by the reaction of chain carriers with impurities or at the wall besides by the union of chain carriers between themselves; namely, the chain may be terminated by the reaction which is of either the first or the second order with respect to the concentration of the chain carrier. It is evident that the reaction which is of the third order or higher with respect to the chain carrier can be neglected. We, therefore, have the following relation after shutting off light.

$$\frac{dC}{dt}=-a\,C-b\,C^2,$$

where C is the concentration of chain carriers, and a and b constants. As the reaction velocity V is proportional to the concentration of chain carriers, we have

$$\frac{dV}{dt}=-AV-BV^2, \qquad (6)$$

where A and B are constants. Integrating (6), we have the relation between the reaction velocity and time; namely,

$$\frac{1}{A}\ln\frac{A+BV}{BV}=t+const.$$

As $V=V_0$ at $t=0$, we have

$$\frac{2.30}{A}\log\frac{V_0(A+BV)}{V(A+BV_0)}=t. \qquad (7).$$

If we can estimate A and B in equation (7), the velocity curve can be plotted. They, of course, can be obtained from the experimental curve of the reaction velocity after shutting off light (Fig. 2); but it is more interesting that the values of A and B can be obtained from the relation between the quantum yield and the reaction velocity in the photostationary state, i. e. from Fig. 4 under the following considerations.

From the equations (5) and (6), we have

$$-AV_t-BV_t^2=-\frac{V_t}{\tau\nu_t},$$

i. e. $$-A-BV=-\frac{19000}{\nu}=-\frac{76000}{\gamma}. \qquad (8)^{28)}$$

This is the relation between the quantum yield γ $(=4\nu)$ and the reaction velocity, and must represent the curve given in Fig. 4; The values of A and B, therefore, can be evaluated from the curve in Fig. 4. We get $A=7.5$ and $B=4.8$ (the unit of the reaction velocity being 10^{-7} mol/sec.). The crosses in Fig. 4, which fall near the experimental curve, are those obtained by equation (8) using these values of A and B.

Putting these values of A and B in (7), we get

$$\frac{2.30}{7.5}\log\frac{V_0(7.5+4.8\,V)}{V(7.5+4.8\,V_0)}=t, \qquad (9)$$

where $V_0=7.14$ for the Expts. I, II and III. This equation must represent the reaction velocity after shutting off light. The values calculated from this equation fall exactly on the experimental curve as indicated by the crosses in Fig. 2. From this we can reversely understand that the extrapolation in Fig. 4 is correct on the whole.

We can also obtain the relation between the reaction velocity and the time during the period of illumination in the following way: here we have evidently

$$\frac{dV}{dt}=N-AV-BV^2, \qquad (10)$$

where N is a quantity which is proportional to the light absorbed in unit time, and A and B are the same as what we have stated above. In the stationary state of Expts. I, II and III, where $V=7.14$, $\frac{dV}{dt}=0$, $A=7.5$ and $B=4.8$, we have $N_{I,II,III}=219$, and we get analogously $N_{IV,V}=121$ and $N_{VI,VII}=39.4$. N's must be proportional to the light absorbed or to the light intensity as the absorption is weak. And indeed we have $\frac{N_{IV,V}}{N_{I,II,III}}=0.40$ and $\frac{N_{VI,VII}}{N_{I,II,III}}=0.13$; and these ratios almost coincide with the corresponding ratios of light intensities, the latter being 0.42 and 0.13 respectively. This coincidence shows us that the above obtained values of A and B are correcet. Now integrating (10) and put-

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28) It is evident that the suffix t can be omitted.

ting $V=0$ at $t=0$, we get

$$\frac{2.30}{Q} \log \frac{(A+2BV+Q)(A-Q)}{(A+2BV-Q)(A+Q)}=t, \tag{11}$$

where $Q\equiv\sqrt{A^2+4NB}$.

The crosses in Fig. 1 are calculated with equation (11) and fall near the experimental curve.

Summary.

1) The photochemical combination of hydrogen and chlorine was investigated by the method of thermal analysis of the velocity of chemical reaction. The changes of the reaction velocity before the photostationary state was reached and after shutting off light were studied. And these changes of velocity were theoretically explained.

2) The mean life of reaction chains and the time taken by a chain link were calculated from the reaction velocity curve after shutting off light, the former being about $\frac{1}{20} \sim \frac{1}{40}$ sec. while the latter $\frac{1}{19000}$ sec. under the experimental conditions. The mean life of reaction chains is in good agreement with that obtained by Weigert and Kellerman by means of the "Schlierenmethode". The collision yield of the partial reaction, $Cl+H_2 \rightarrow HCl+H$, was calculated to be 10^{-5}, which agrees with the results obtained by Rodebush and Klingerhöfer in a different way.

3) The concentration of chlorine atoms in the photostationary state was calculated. In agreement with Chapman and Gibbs, and Ritchie and Norrish, the velocity of hydrogen chloride formation is proportional to a power of the intensity of light approaching 0.5 (actually 0.6). The reaction chains are thus terminated mainly by self-neutralisation, but it is unlikely that these chain terminating reactions are of the triple collision type such as $Cl+Cl+M \rightarrow Cl_2+M$.

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The Laboratory of Physical Chemistry,
Kyoto Imperial University.