PHOTOCHEMICAL INTERMITTENCY

AND THE

PHOTOCHLORINATION OF TETRACHLOROETHYLENE

IN CARBON TETRACHLORIDE SOLUTION

Thesis by

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INTRODUCTION

If a photochemical reaction involving an intermediate step or steps proceeds at a rate proportional to the rate of absorption of light to some power other than one, it is readily seen that if intermittent insolation is used, the reaction-rate will be a function of the frequency thereof. For, speaking rather loosely, intermittent light of frequency very high compared to the duration of the intermediate processes of the reaction will be in effect continuous light of a certain intensity; whereas intermittent light of very low frequency will produce effectively alternate light and dark periods, the former of a higher intensity than the "continuous" radiation. Although the total amount of radiation absorbed is the same in both cases, different rates will be obtained because of the non-linear dependence upon light intensity.

The work to be described was undertaken to verify the general results predicted by the intermittency theory as developed below, and to obtain some notion of the rate-constant of the assumed intermediate step in the particular reaction studied. This last possibility is perhaps the most useful and interesting feature of the intermittency effect, since it puts one in perhaps a more favorable position to discuss the mechanism of the reaction.

THEORETICAL

A. Derivation of the reaction rate under intermittent
   illumination.

   We shall consider the following general reaction:

$$A_2 + h\nu \rightarrow 2A \qquad\qquad k_1.$$

$$A + B \rightarrow C + A \qquad\qquad k_3.$$

$$2A \rightarrow A_2 \qquad\qquad k_4.$$

Now $-\dfrac{d(B)}{dt} = k_3 (A)(B).$ $\qquad\qquad$ (1)

$+\dfrac{d(A)}{dt} = 2 (I_{abs.}),$ assuming for the moment that
each light quantum absorbed produces dissociation.

$$-\frac{d(A)}{dt} = 2 k_4 (A)^2$$

In the steady state evidently

$$(A) = (I_{abs.})^{1/2} k_4^{-1/2}.$$

whence finally

$$-\frac{d(B)}{dt} = \frac{k_3}{\sqrt{k_4}} (B)(I_{abs.})^{1/2} \qquad\qquad (2)$$

where $(I_{abs.})$ is the rate of absorption of
radiation in einsteins per liter minute.

However, if the illumination is intermittent
(we shall assume uniformity of intermittency; i.e., all
light periods are equal in duration, as are the dark
periods), we must write two differential equations, one
for the light period and one for the dark:

Light: $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (∅)

$$\frac{d(A)}{dt} = 2(I_{abs.}) - 2 k_4 (A)^2 \qquad\qquad (3)$$

Separating the variables and integrating,
we find:

$$\sqrt{\frac{k_4}{(I_{abs.})}} \, \tanh^{-1}\left[(A)\sqrt{\frac{k_4}{(I_{abs.})}}\right] = 2k_4 t + const.$$

Letting $\alpha = \sqrt{\frac{k_4}{(I_{abs})}}$ for convenience in
writing, we have:

$$\alpha \tanh^{-1}\left[\alpha(A)\right] = 2k_4 t + const. \qquad (4)$$

Dark: $\dfrac{d(A)}{dt} = -2k_4(A)^2 \qquad\qquad (5)$

Again integrating, we have:

$$\frac{1}{(A)} = 2k_4 t + const.' \qquad\qquad (6)$$

It is evident that the concentration of A
builds up in the light and decays in the dark in such a
manner as indicated in figure 2, (figure 2 will be dis-
cussed in detail later), ultimately reaching a steady
state, wherein the decay exactly balances the growth.
Leaving for the moment the question of how soon this
steady state is reached, we shall enquire into the
limiting values of (A) after it has been attained.

Steady Illumination: Placing $t=0$ when $(A)=0$
in equation (4),

we find const. $=0$, whence

$$(A) = \frac{1}{\alpha} \tanh\left[\frac{2k_4 t}{\alpha}\right]$$

$$\text{As } t \to \infty, \ (A) \to \frac{1}{\alpha} = \sqrt{\frac{(I_{abs})}{k_4}} \qquad (7)$$

Intermittent Illumination With Very Long Periods.

Let τ and $n\tau$ be the durations of light and dark periods respectively. It is readily seen from the figure
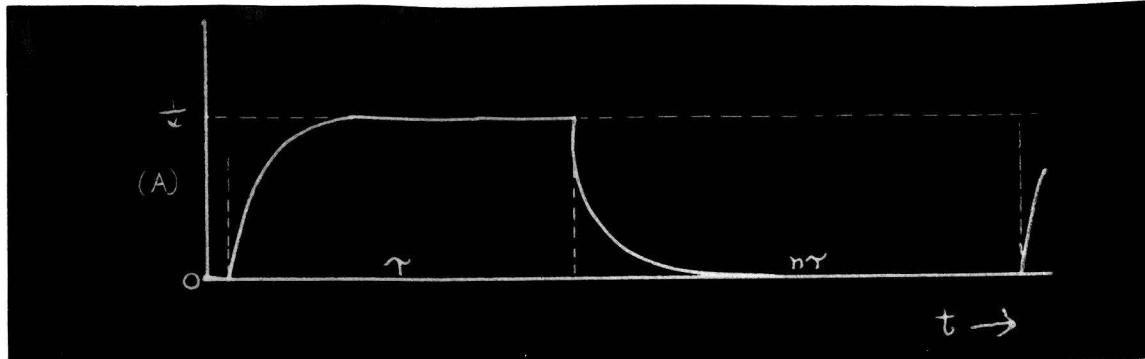
that the average value of (A) is the area under the curve for one cycle, divided by $\tau + n\tau$. In the limit this is seen to be:

$$\frac{1}{\tau + n\tau}\left(\frac{1}{\alpha}\tau + 0\right) = \frac{1}{n+1} \cdot \frac{1}{\alpha} \tag{8}$$

Intermittent Illumination With Very Short Periods.

(A) will evidently reach a steady state when

$\tau \times$(slope of light curve vs. time)

$= n\tau \cdot (-$ slope of dark curve). These slopes are given directly by equations (3) and (5), which solve to

$$(A) = \sqrt{\frac{(I_{abs.})}{k_4(n+1)}} = \frac{1}{\sqrt{n+1}} \cdot \frac{1}{\alpha} \tag{9}$$

Thus if a rotating sector is used to produce the intermittency, for a 1:1 sector we have from (8) and (9), if $\bar{A}$ = average value of (A),

Slow rotation : $\bar{A} = \frac{1}{\alpha} \cdot \frac{1}{2}$

Fast rotation : $\bar{A} = \frac{1}{\alpha} \cdot \frac{1}{\sqrt{2}}$

And for a 1 ⦂ 3 sector, i.e., light:dark = 1 ⦂ 3, we have

$$\text{Slow rotation : } \bar{A} = \frac{1}{2} \cdot \frac{1}{4}$$

$$\text{Fast rotation : } \bar{A} = \frac{1}{\alpha} \cdot \frac{1}{2}$$

But from (1) we see that for given values of (B) and (I abs.) the overall reaction rate is proportional to $\overline{(A)}$. We must then derive an expression for $\bar{A}$ under varying conditions of (I abs), h, and γ.
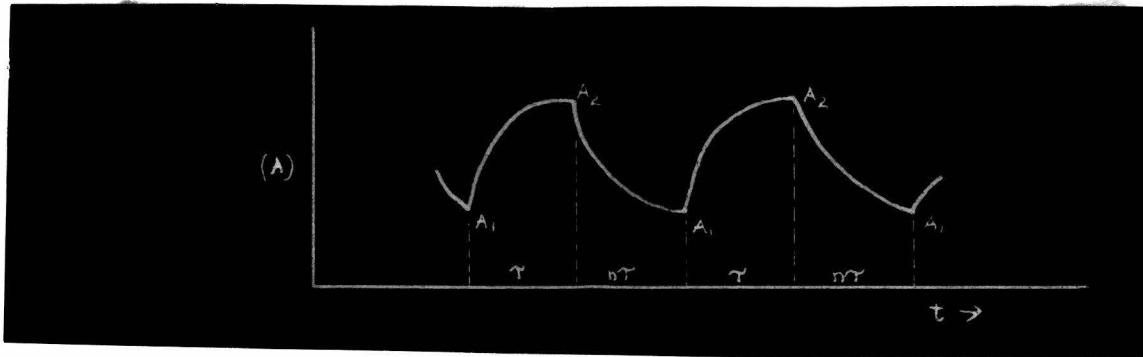
From the figure , which is drawn for a steady state, $\bar{A}$ is evidently the area under two consecutive segments of the curve divided by $\gamma + n\gamma$.

Light Period

$$\text{Area} = \int_{t}^{t+\gamma} (A)\, dt$$

Changing the variable from t to (A) by means of (3), and omitting parentheses on (A) henceforth, we have

$$\frac{1}{2k_4} \int_{A_1}^{A_2} \frac{\alpha A}{1-\alpha^2 A^2} \, d(\alpha A) \tag{10}$$

where as before

$$\alpha = \sqrt{\frac{k_4}{(I_{abs.})}}$$

This gives on integration

$$\frac{1}{2k_4} \log_e \left(\frac{1-\alpha^2 A_1^2}{1-\alpha^2 A_2^2} \right)^{1/2}$$

Dark Period   Using (5) we have

$$\int_{t+\gamma}^{t+(n+1)\gamma} A\,dt = -\frac{1}{2k_4} \int_{A_2}^{A_1} \frac{A}{A^2}\,dA = \frac{1}{2k_4} \log_e \frac{A_2}{A_1} \tag{11}$$

Adding (10) and (11) and dividing by $(n+1)\gamma$,

we have

$$\bar{A} = \frac{1}{2k_4\gamma(n+1)} \log\left[\left(\frac{1-\alpha^2 A_1^2}{1-\alpha^2 A_2^2}\right)^{\frac{1}{2}} \cdot \frac{A_2}{A_1}\right] \tag{12}$$

Now putting limits into (4) and (6) we may write

$$\tanh^{-1}[\alpha A_2] - \tanh^{-1}[\alpha A_1] = \frac{2k_4}{\alpha}\gamma \tag{13}$$

$$\frac{1}{A_1} - \frac{1}{A_2} = 2k_4 n\gamma \tag{14}$$

Letting $x = \sqrt{4k_4(I_{abs.})}\,\gamma$, we may eliminate A_1

from (12) using (13) and (14). The result is:

$$\bar{A} = \frac{1}{2k_4\gamma(n+1)}\left[x + \log_e\left(1 + \frac{nx}{1 + \frac{1}{\alpha A_2}}\right)\right] \tag{15}$$

It is of interest to note that αA_2 is the

steady state value of A_2 for any given x divided

by the maximum value of A for steady illumina-

tion. Now what we shall measure is the ratio

of the rates of reaction under a given speed

of rotation and under steady illumination,

which ratio equals $\dfrac{\bar{A}}{A_{steady}}$. Since $A_{steady} = \sqrt{\dfrac{(I_{abs.})}{k_4}}$

from (7), we may write

$$\frac{\bar{A}}{A_{steady}} = \frac{1}{(n+1)x}\left[x + \log\left(1 + \frac{nx}{1 + \frac{1}{\alpha A_2}}\right)\right] \tag{16}$$

It is possible to solve (13) and (14) for αA_2. The result is:

$$\alpha A_2 = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where
$$a = (nx - 1) + (nx + 1)e^{2x}$$
$$b = nx(1 - e^{2x})$$
$$c = 1 - e^{2x}$$

(17)

We may then obtain a plot of $\dfrac{\tilde{A}}{A_{steady}}$ vs. x for any given n by obtaining αA_2 from (17) and substituting the value into (16). Figure I shows such a plot for n = 3, the value used in the experimental work to be described.

A table of $\dfrac{1}{\alpha A_2}$ and $\dfrac{\tilde{A}}{A_{steady}}$ for selected values of x follows:

TABLE I

x	$\dfrac{1}{\alpha A_2}$	$\dfrac{\tilde{A}}{A_{steady}}$
0.01	1.985	0.4999
0.10	1.858107	0.4995335
0.20	1.732	0.498
0.50	1.4457	0.48914
1.00	1.1811	0.466
2.00	1.024	0.422
3.00	1.004	0.392
5.00	1.00057	0.3572
10.00	1.0000	0.3192
14.00	1.0000	0.3052
20.00	1.0000	0.2925
22.00	1.0000	0.290
26.00	1.0000	0.285
30.00	1.0000	0.282
34.00	1.0000	0.279
40.00	1.0000	0.2757
100.00	1.0000	0.2625
500.00	1.0000	0.2533

We must now determine how soon after the start of illumination the steady state for (A) is reached. We may derive from (4), setting $t=0$ when $\alpha A = 0$, and from (6), setting $t=0$ when $\alpha A = 1$, the following expressions:

Light Period: $\alpha A = \tanh\left[x\frac{t}{\tau}\right] = \tanh\left[\sqrt{4(I_{abs.})k_4}\, t\right]$

Dark Period: $\alpha A = \dfrac{1}{x\frac{t}{\tau}+1} = \dfrac{1}{\sqrt{4(I_{abs.})k_4}\, t + 1}$

which expressions are free from τ, as is clear they must be. We may then plot curves for (A) against $x\frac{t}{\tau}$ for any desired values of n and x, and starting with (A) = 0 when t = 0. This has been done in figure 2, where the larger segmented curve is for x = 1, the smaller for $x = \frac{1}{10}$, and n = 3 in both cases. The dotted lines indicate the upper limits in the steady states. It is thus seen that if x is varied from 1 to $\frac{1}{10}$ by changing τ only, the steady state is quickly reached in about the same length of time in each case, which time is quite short. It is seen that because the growth curve is a hyperbolic tangent, for x = 5 αA has attained 99.99% of its maximum value when t = τ, i.e. at the close of the first light period. Further, it is seen from figure 1 that the optimum range of x to work in lies to the right of x = 1; so that one or two revolutions of the sector will suffice to effect a steady state for (A).

It is to be noted that the dimensions of x are those of pure number.

B. The Reaction Studied

The photooxidation and photochlorination of tetrachloroethylene have been studied by Dickinson and his co-workers.[1,2,3] It has been found that chlorination does not sensibly proceed until all the oxygen present has been reduced by a chlorine sensitized oxidation. The chlorination then takes place substantially in accordance with the equation:

$$- \frac{d(Cl_2)}{dt} = k(I_{abs.})^{1/2}(Cl_2) \tag{18}$$

This reaction will presently be treated in detail.

EXPERIMENTAL

A. Apparatus.

The source of light was an atmospheric pressure mercury lamp, air-cooled, which was found to have a surface intensity of $\lambda 4358$ of 6 or 8 times that of an ordinary commercial evacuated arc, when operating with half the power consumption of the latter. A portion of the arc 4x9 mm was used; light from this passed thru the sector (placed quite close to the arc), then thru a water-cooled filter which isolated $\lambda 4358$ by means of Corning

1. Dickinson and Leemakers J.A.C.S 54   3852 (1932)

2. Leermakers and Dickinson   "   54   4648 (1932)

3. Dickinson and Carrico   "   56   1473 (1932)

glasses Noviol A and blue purple ultra, and 12 mm. of
1 m. Cu_2SO_4.

The light was collimated by a pair of 8 diopter
lenses, placed after the filters, after which a portion
of the light was reflected off at right angles by two
parallel glass plates. This reflected light passed thru
a compensating tank of xylene and on to a thermopile.
The direct beam passed into the thermostat, a brass box
filled with three windows. Two diaphragms were provided;
one of 35 mm. integral with the box, and one of 12 mm.
which could be slipped into a position concentric with
the other. The light finally passed out onto a second
thermopile.

The reaction cell employed was of pyrex glass
of the shape below:
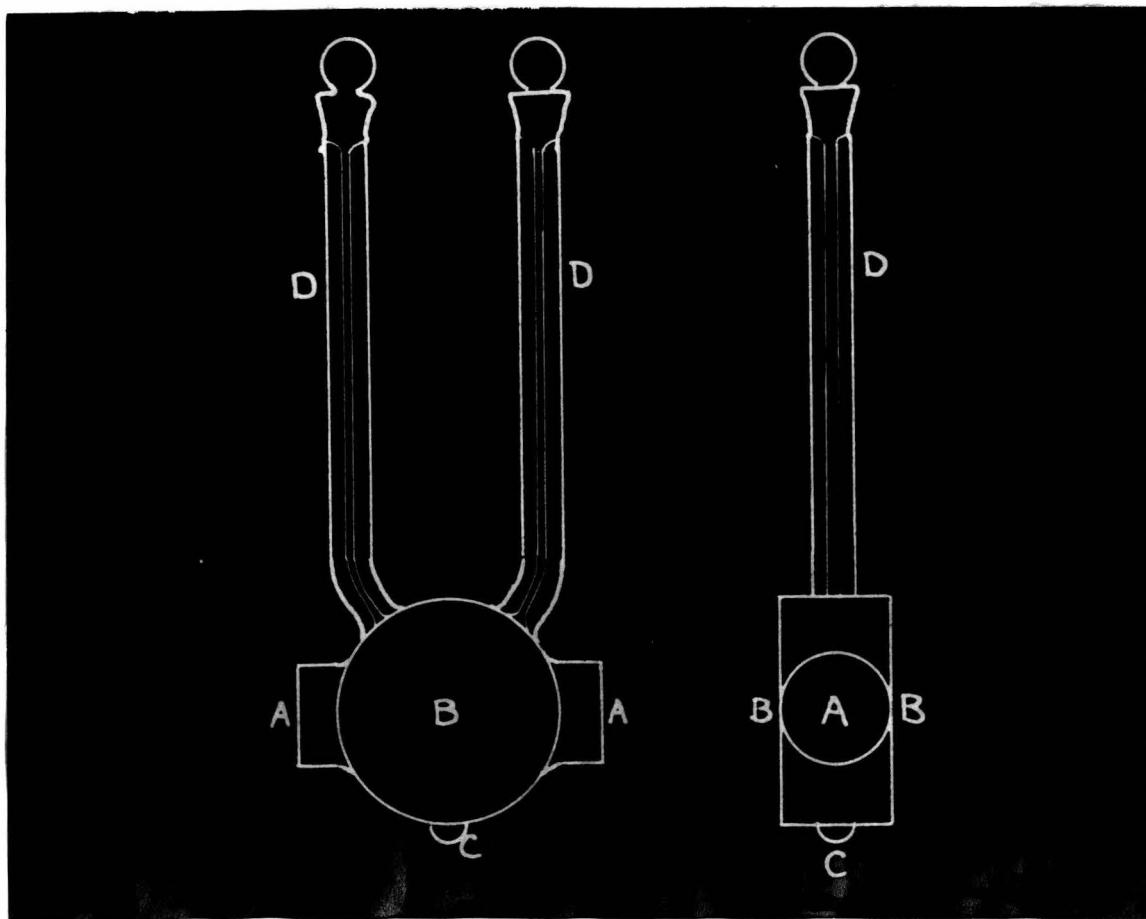
The A's and B's are flat glass plates, with AA = 5.36 cm. and BB = 1.44 cm. Thus there is a considerable range of chlorinee concentration (0.070 m. to 0.014 m.) in which the absorption of λ4358 for the short path is less than thirty percent while transmission for the long path is less than 70%. Thus it was advantageous to carry out the reaction passing light thru the faces B (diam. of beam 35 mm.) and to measure the chlorine concentration by transmission measurements thru the faces A (diam. of beam 12 mm.). A mirror was placed behind one of the faces B when the reaction was being carried out, thus maintaining a substantially uniform intensity of radiation thruout the cylinder illuminated. The cell was so mounted that it could be easily turned through 90º ; in each position one of the faces A or B was within a few millimeters of the diaphragm used.

A glass bead C was enclosed in the cell to provide stirring. Long capillary tubes D made possible relatively permanent removal of exygen from the main body of the cell.

The rotating sector was driven by a synchronous motor thru a gear chain. Eighteen different sector speeds of from 1.736 to 562.5 r.p.m. were possible. All of the work to date has been carried out with a one to three sector.

The tank was provided with a stirrer, heating coil, and thermometer. The tank was filled with xylene,

xylene, glass and carbon tetrachloride having nearly the same indices of refraction.

Preliminary illumination was carried out thru a window in one end of the box by means of a 500 watt projection lamp, a one inch layer of 10% cupric chloride solution serving as an infra red filter.

The filter system was found to be effective by spectroscopic examination; the apparatus was tested as a photometer with $K_2 Cr O_4$ and proved satisfactory. The absorption coefficient of Cl_2 in CCl_4 was determined; subsequent titration of the solutions gave $\varepsilon = 2.17$ defined by $\frac{I}{I_0} = 10^{-\varepsilon c d}$ (in mols/liter, d in cm.). Leermakers and Dickinson[2] found 2.14; Dickinson and Leermakers[1] found 2.26. Beer's Law was tested by a dilution of the solution used within the range of Cl_2 concentrations subsequently employed and found to hold.

The chlorine, CCl_4, and C_2Cl_4 were purified as described by Dickinson and Leermakers.[1]

The thermopiles were connected to two D'Arsonval galvanometers with a common scale. The galvanometers were tested for linearity and proper corrections were applied to all readings. During the experiments illumination was provided by a yellow safelight found to transmit no visible radiation absorbable by chlorine.

The experiments were carried out as follows: Known amounts of C_2Cl_4 and Cl_2 in CCl_4 were diluted with CCl_4 to a known volume; the cell was filled, and after

in some cases preliminary exposure to sunlight for $\frac{1}{2}'$
to 1' exposed to the projection lamp, with shaking every
minute. The Cl_2 concentration was followed by means of
an automobile headlight bulb replacing the mercury lamp.
As soon as the former began to diminish, short exposures
with careful shaking were made until it was ascertained
that the chlorine was disappearing uniformly, thus insuring
complete removal of oxygen.

The mercury lamp was then started, and the
Cl_2 measured, using three 20" exposures thru the long
path. Illuminations of from 3' to 12' were made, usually
each at a different sector speed. "Infinite" sector
speed was obtained usually by means of a wire screen
of 24% transmission. The chlorine concentration was
of course determined between each run, and the solution
was stirred before and after each determination.

It was found possible to make a satisfactory
correction for the reaction caused by the measurements
of Cl_2 concentration, since each succeeding galvanometer
swing was found to suffer a nearly constant increment.
Correction was also made for the unilluminated portion
of the solution under the assumption that no mixing
occurred during the run, an assumption which of course
became less valid as the time of the run was increased.

TREATMENT OF DATA

If I_c is the sensibly constant (because of

the mirror) intensity of illumination prevailing thruout the solution, we may readily derive the following expression:

$$(I_{abs.}) = I_c \cdot \varepsilon \cdot (Cl_2) \cdot \Delta x \cdot \log_e 10.$$

where Δx is the path length. If I_0 is further the number of einsteins per minute entering the reaction vessel from the lamp, we may set

$$I_c = \beta I_0$$

where β is evidently a function of the transmission of the solution. Taking 0.875 as the reflective power of silver for $\lambda 4358$, we may derive the following empirical expression for the average β corresponding to a given (Cl_2):

$$\beta = 1.875 - 12.7 (Cl_2) + 50.6 (Cl_2)^2.$$

We then may derive the following expression:

$$(I_{abs.}) = \frac{(Cl_2) \cdot \beta \cdot I_0 \cdot \varepsilon \cdot \Delta x \cdot \log_e 10}{\text{volume in liters}} \tag{19}$$

We may integrate the rate expression given by (18), regarding β as constant thruout a run. (The small variation in β is overshadowed by variations in I_0, for example.) We derive the following expression:

$$k = \frac{\dfrac{1}{(Cl_2)_2^{1/2}} - \dfrac{1}{(Cl_2)_1^{1/2}}}{11.4 \sqrt{\beta I_0} \, \Delta t}$$

where Δt is the time of the run in minutes.

The data of a sample experiment (5-12a) are reproduced below, where I_0 (and thus k) is expressed in arbitrary units (cm. of galvanometer deflection.)

TABLE II

(Cl_2) before illumination = 0.1585 m.

(C_2Cl_4) " " 1.370 m.

Temp. 25.0 - 26.0° C.

Run	γ	Δt	I_0	Av. I_0	(Cl_2)	$(Cl_2)_2^{-1/2}-(Cl_2)_1^{-1/2}$	Av. β	k
1	0	3.00'	4.78	4.58	.0847	0.856	1.24	0.0105
			4.81		.0543			
2	1/20.85	3.06'		4.70	.0634	0.630	1.34	0.0072
			4.58		.0462			
3	0	3.25'		4.38	.0509	0.959	1.43	0.0104
			4.54		.0339			
4	1/46.88	4.09'		4.54	.0387	0.822	1.51	0.0067
			4.53		.0231			
5	0	7.50'		4.40	.0310	2.073	1.60	0.0091
			4.64		.0164			
6	1/46.88	9.47		4.65	.0206	1.926	1.68	0.0064
			4.66		.0124			

The runs with $\gamma = 0$ were with a screen of 24%
transmission; the av. I_0 was thus reduced by 4% to
correspond to a 25% sector of infinite speed of rotation.
The fact that the (Cl_2) is less at the end of one run
than at the beginning of the next arises from the mixing
of presumably unilluminated reactants between runs by
shaking.

From a cause not understood, but due perhaps
in part to convection in the solution during the run and
in part to approximations in the method of treatment
which were well nigh unavoidable, the k's found with the

screen, which should have been constant, fell off with
decreasing chlorine concentration and with increasing Δt.
The decrease was as much as 18% for the very lowest (Cl_2)
and longest runs. This phenomenon appeared to be a func-
tion of both Δt and (Cl_2), for when an experiment was
carried out in which as the (Cl_2) diminished the length
of the runs was also diminished, thus reversing the
usual treatment, the k's tended to be constant. This
was apparently not due to a lack of C_2Cl_4, for Leermakers
and Dickinson observed no such effect working with the
same amounts of Cl_2 and C_2Cl_4 ; further, increasing the
ratio of C_2Cl_4 to Cl_2 initially present by a factor
of two in one experiment (5-18a ; see table III) caused
no difference in behavior. Thermal reaction of appre-
ciable magnitude would have caused an increase in the
k observed with increasing time of run, instead of a
decrease. The effect was still present when the k's
were calculated neglecting the rather large correction
for unilluminated solution.

No correction was made for thermal reaction;
this was assumed to be negligibly small, in accordance
with the results of Leermakers and Dickinson. These
workers found the thermal rate to be of such a magnitude
that probably less than 1% of the change of chlorine
concentration in the present experiments could be
ascribed to this source.

A highly empirical but practicable method of

correlating the various k's for $\gamma = 0$ with Δt and (Cl_2) was found to be the following: The k's are plotted against $(Cl_2)/\Delta t$. All of the points corresponding to a given Δt are then found to lie on nearly straight lines, all of which have the same general slope. By this device we can then calculate what the k for $\gamma = 0$ would have been for any particular run in which the sector was rotated at a finite rate.

Thus for each such run a value of $\dfrac{\bar{A}}{A_{steady}}$ ~~steady~~ was obtained. It will be recalled from our previous deviations that for a 1:3 sector $\bar{A}/A_{steady}$ varies from 0.50 to 0.25 as γ goes from 0 to ∞. This was found to be the case. Since $x = \sqrt{4 k_4 (I_{abs})} \gamma$ and $\log x = \log 2 + \log \sqrt{k_4} + \log(\sqrt{I_{abs}}\, \gamma)$, k_4 can be found by the difference in abcissae required to bring about coincidence of a plot of $\log x$ vs. $\bar{A}/A_{steady}$ as calculated from figure I, and a plot of $\log(\sqrt{I_{abs}}\, \gamma)$ vs. $\bar{A}/A$ steady as determined from experiment. Such a plot, with the curve in the position chosen as best, is shown by figure 3.

There follows a table presenting the essential data of the individual experiments. For those runs where $\gamma \neq 0$, $\log(\sqrt{I_{abs}}\, \gamma)$, the calculated k for $\gamma = 0$, and the value of $\bar{A}/A$ steady therefrom are given. Columns 2 and 3 give the concentrations of chlorine and tetrachloroethylene in mols per liter with which the solution was made up; columns 4 and 5 the average intensity (in cm. of galvanometer deflection) and chlorine concentration

prevailing during each run; column 6 the reciprocal of
the duration of the light flash in minutes; column 7
the duration of the run in minutes, column 8 the observed
reaction rate constant, (Iabs) being expressed in cm.
of galvanometer deflection, column 9 the calculated k
which would have obtained under similar conditions but
with infinitely fast sector rotation, column 10 the sum
of the logarithms of the square root of (Iabs) (the
particular values quoted must be multiplied by $\log_e 10$
and divided by the volume of illuminated solution in
liters, and moreover include I_0 expressed in cm. of
galvanometer deflection) and γ, and column 11 the ratio
of the rate observed to the rate under similar conditions
but without the sector.

TABLE III

Expt.		(Cl_2)	(C_2Cl_4)	I_0	(Cl_2)	$1/\tau$	Δt	k	$k(\tau=0)$	$\log(\sqrt{I_{abs}}\,\tau)$	$\bar{A}/A_{steady}$
4-24a	1	0.1220	0.783	4.23	.0563	∞	3'	.01015			
	2			4.23	.0405	2250	4.05'	.01122			
	3			4.23	.0292	∞	5'	.00985			
	4			4.42	.0209	2250	6'	.00970			
	5			4.37	.0140	∞	8'	.01118			
4-25a	1	0.1220	0.783	4.25	.0481	∞	3'	.01020			
	2			4.23	.0355	750	5'	.00976	.01057	$\bar{3}.0488$	.457
	3			4.07	.0251	∞	6'	.00908			
	4			4.34	.0167	750	9'	.00973			
	5			4.42	.0112	1/4	16'	.00523			
4-30a	1	0.1220	0.783	4.35	.0451	∞	3'	.00953			
	2			4.57	.0333	333	4½'	.00970	.01010	$\bar{3}.4014$	.480
	3			4.46	.0243	1667	5½'	.00795	.00933	$\bar{3}.6435$	.427
	4			3.94	.0172	∞	8'	.00901			
4-30b	1	0.1220	0.783	4.10	.0593	1667	3'	.00874	.01025	$\bar{3}.7767$	.425
	2			4.03	.0468	333	3'	.00920	.00979	$\bar{3}.4346$	.469
	3			3.91	.0360	1667	4'	.00926	.01025	$\bar{3}.6866$	.451
	4			3.72	.0268	∞	5'	.00997			
	5			4.60	.0188	333	7.17'	.00914	.00840	$\bar{3}.3032$	
	6			5.00	.0130	∞	8'	.00895			
5-4a	1	0.1220	0.783	4.05	.0388	4688	4'	.00814	.01047	$\bar{2}.2577$	.390
	2			3.89	.0283	∞	6'	.00936			
	3			3.96	.0195	9372	9'	.00779	.00933	$\bar{3}.8293$	.428
	4			3.75	.0130	∞	12'	.00815			
5-5a	1	0.1587	1.175	5.36	.0421	4688	3.98'	.00668	.01057	$\bar{2}.3324$	.316
	2			4.68	.0296	∞	6'	.01010			
	3			4.64	.0207	4688	9.13'	.00572	.00933	$\bar{2}.5263$	.306
5-7a	1	0.1587	1.370	5.28	.0283	4688	6.05'	.00764	.00995	$\bar{2}.2589$	.384
	2			4.73	.0196	∞	7.04'	.00849			
	3			4.76	.0149	4688	8.9'	.00423	.00870	$\bar{2}.1186$	.242
5-12a	1	0.1587	1.370	4.58	.0695	∞	3'	.01053			
	2			4.70	.0540	2085	3.06'	.01000	.01019	$\bar{2}.6955$	.354
	3			4.38	.0419	∞	3.25'	.01034			
	4			4.54	.0329	4688	4.09'	.00675	.00990	$\bar{2}.2543$	.339
	5			4.40	.0234	∞	7.50'	.00914			
	6			4.65	.0162	4688	9.47'	.00637	.00879	$\bar{2}.1287$	.362
5-13a	1	0.1587	1.370	4.76	.0657	2085	3.07'	.00690	.01048	$\bar{2}.7267$	.329
	2			4.47	.0507	∞	3'	.01038			
	3			4.50	.0385	9375	4'	.00840	.01040	$\bar{3}.9782$	.401
	4			4.25	.0281	∞	5'	.01018			
	5			4.47	.0176	9375	8.02'	.00758	.00898	$\bar{3}.8363$	.422

TABLE III (Cont'd)

Expt.	(Cl_2)	(C_2Cl_4)	I_0	(Cl_2)	$1/\gamma$	Δt	k	$k(\tau=0)$	$\log(\sqrt{I_0}\gamma)$	A/A_{steady}
5-18a 1	0.0900	1.568	4.58	.0378	∞	4'	.01038			
2			4.60	.0282	4688	5.54'	.00695	.00996	$\overline{2}.2304$	.350
3			4.23	.0203	∞	7.17'	.00673			
4			4.28	.0152	4688	7.51'	.00581	.00867	$\overline{2}.0997$	.334
5-25a 1	0.1587	1.370	1013	.0598	∞	6.5'	.00979			
2			0903	.0448	∞	9'	.00839			
3			3.70	.0316	∞	6'	.01017			
4			1552	.0226	∞	3'	.00885			
5			1552	.0160	∞	$3\frac{1}{2}$'	.00985			
6			1594	.0124	∞	$3\frac{1}{2}$'	.0056			

No determination was made of the absolute light
intensity corresponding to unit galvanometer deflection;
instead this quantity was calculated from the rate con-
stant determined by Leermakers and Dickinson[2]. When
this value (5.1 in mols, einsteins, liters, and seconds)
is used it is found that one cm. of galvanometer deflec-
tion, that is, one unit of I_o as used above, corresponds
to a total flux of 6.54×10^{-8} einsteins per minute
entering the reaction cell when the 35 mm. diaphragm
is employed, if we take as a mean reaction rate con-
stant .0101 in the arbitrary units heretofore used.
Using the same beam splitting device and the same galva-
nometers and thermopiles, though possibly in a permuted
arrangement, Leermakers and Dickinson found a flux of
13.56×10^{-8} einsteins per minute passing an equal area
in a similar position. This difference could probably
easily be accounted for if we take into consideration
the different sensitivities of the thermopiles and
galvanometers, and the variation caused by slight changes
in alignment of the different pieces of apparatus.

Using then the value thus obtained for the
absolute light intensity, we readily find from figure
3 the following values of k_4, where the first column of
figures gives the difference in abcissae of the calculated
curve and of the plot of the group of points (τ is in
minutes, and (I_{abs}) is only partially converted to cm. of
galvanometer intensity, as explained in connection with

column 10 of Table III), and the second column the values

of k_4 in cubic centimeters per mol second:

TABLE IV

	Difference in logarithms	k_4
Best fit	-3 + 0.50	3.7×10^{11} c.cm/mol sec.
Extremes:	-3 + 0.38	2.5×10^{11}
	-3 + 0.60	6.6×10^{11}

DISCUSSION OF RESULTS

Two mechanisms have been proposed for the

reaction studied[2]   They are:

Mechanism A

$$Cl_2 + h\nu \rightarrow 2\ Cl \tag{1}$$

$$Cl + C_2Cl_4 \rightarrow C_2Cl_5 \tag{2}$$

$$C_2Cl_5 + Cl_2 \rightarrow C_2Cl_6 + Cl \tag{3}$$

$$2\ C_2Cl_5 \rightarrow 2\ C_2Cl_4 + Cl_2 \quad (or\ C_2Cl_6 + C_2Cl_4) \tag{4}$$

Mechanism B

$$Cl_2 + h\nu \rightarrow 2Cl \tag{1}$$

$$Cl + Cl_2 \rightarrow Cl_3 \tag{2}$$

$$Cl_3 + C_2Cl_4 \rightarrow C_2Cl_6 + Cl \tag{3}$$

$$2\ Cl \rightarrow Cl_2 \tag{4}$$
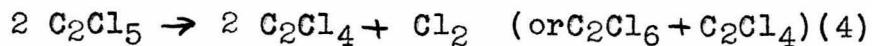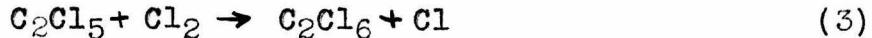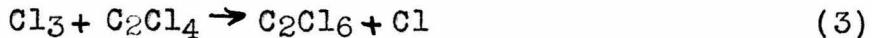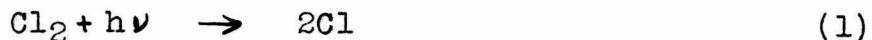
Now it will be recalled that k_4 was obtained from an ex-

pression of the type $\sqrt{k_4 I_{abs} \gamma}$, under the assumption that

the quantum yield of the first reaction in the mechanisms

above was unity. It is readily seen, however, that if

this is not the case, the values of k_4 above are really those for r_1k_4, where r_1 is the primary quantum yield. The much disputed question of the actual occurrence of such a "primary recombination" of halogens in solution has not been settled[4]. The presumption is of course that the dissociated atoms recombine before they have had a chance to become separated by diffusion.

We may calculate in the usual way (see for example ref. 3) the specific collision rates at 25° for the reactions of interest in the mechanisms above. Using the estimated molecular diameters of Dickinson and Carrico[3] and taking 5.8 Å as the diameter of Cl_3, we find the following collision rates, in mols, c.cm., and seconds:

	Mechanism A	Mechanism B
$k_3{}^0$	2.0×10^{14}	2.1×10^{14}
$k_4{}^0$	9.5×10^{13}	16.4×10^{13}

If r_4 is the fraction of collisions of the reactants in (4) which are effective in producing combination, we may readily derive the following, using the "best" value of r_1k_4 from Table IV:

$$r_1 r_4 = \frac{1}{260} \quad \text{(Mech. A)}; \quad r_1 r_4 = \frac{1}{440} \quad \text{(Mech. B)}$$

Thus r_1 and r_4 lie somewhere between unity and $\frac{1}{260}$ or $\frac{1}{440}$ depending on the mechanism chosen, and subject to the restraint of the equations above. There is no reason to suppose that r_1 and r_4 are greater than unity.

4. Franck and Rabinowitch: Trans. Far. Soc., 30, 120 (1934)
   Ogg: Chem. Reviews, 17 423 (1935)
   Rabinowitch and Wood, Trand. Far. Soc. 32, 555 (1936)

Dickinson and Carrico[3] have given an exhaustive analysis of the two mechanisms in terms of collision rates and collision efficiency. They were unable to make a choice between the two mechanisms on the basis of the data at hand. The partial knowledge gained in this experiment concerning the quantities of interest does not yet permit a conclusive statement to be made concerning which mechanism is the more likely.

Further work on the problem will perhaps include a determination of the temperature coefficient of k_4 ; a more precise determination of the thermal reaction; use of sectors of different ratios of light and dark periods; actual determination of the absolute amount of radiation entering the reaction-cell, and an investigation of the cause of the observed falling-off of the rate constant. It is not unlikely that the question of primary recombination of halogens will be settled before long, in which case the actual k_4 determined in this experiment will be more precisely known.

SOURCES OF ERROR

The principal uncertainty in the measurements arose in the chlorine concentration measurements. Galvanometer drift, unknown amounts of convection within the solution, and slight fluctuations of lamp intensity during the measurement combined to make the accurate

determination of a second-order effect such as the one under investigation difficult. This was particularly so under conditions of low chlorine concentration, of course.

The fluctuation of the lamp during a run likewise led to uncertainty in the results, although this did not appear to have been a difficulty of first magnitude. The method of treating the data by taking an average of radiation intensity and chlorine concentration in order to calculate (I_{abs}) probably did not introduce serious error, nor did the assumption of uniform intensity thruout the solution.

Dark reaction has been mentioned as considered negligible.

Convection and mixing of the solution was an unknown factor; but calculation of reaction rate constants under the assumption of complete mixing and under the assumption of no mixing did not lead to widely different results.

No great lack of uniformity of intensity over the cross section of the beam was apparent; however, this will be investigated later.

ACKNOWLEDGEMENT

SUMMARY

The theory of intermittency in certain types of photochemical reaction has been developed. A relation between reaction rate and certain experimental variables has been explicitly derived for illumination through a 90 degree sector.

The determination of the rate constant of the chain breaking step in the photochlorination of tetrachlorolthylene in carbontetrachloride solution has been made; the most probable value is $k_4 r_1 = 3.7 \times 10^{11}$ c cm/mol second, where k_4 is the rate constant and r_1 is the quantum yield of the primary photochemical process. r_1 has been shown to lie probably between 1 and 1/260 or 1/440, depending on which of two mechanisms proposed is chosen.

Sources of error are discussed.
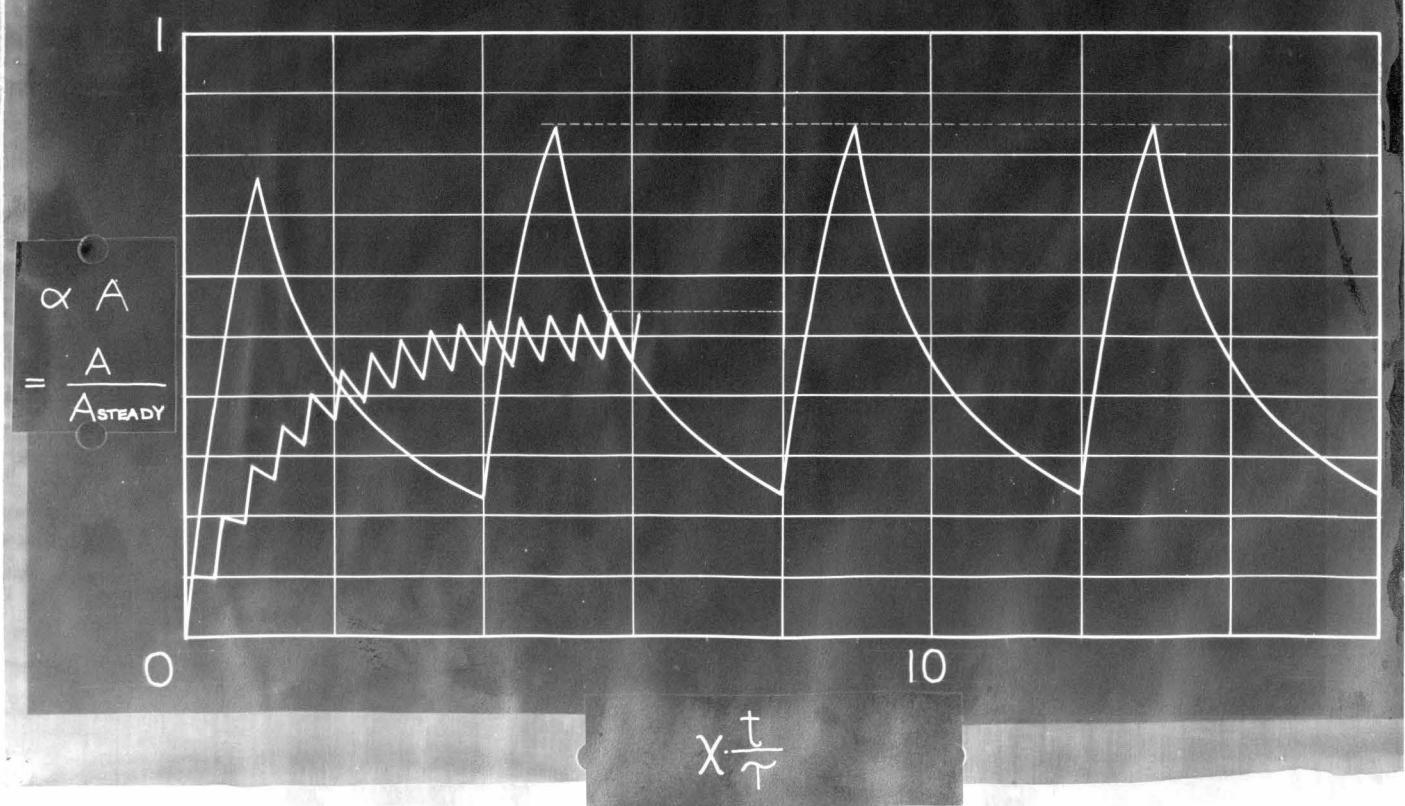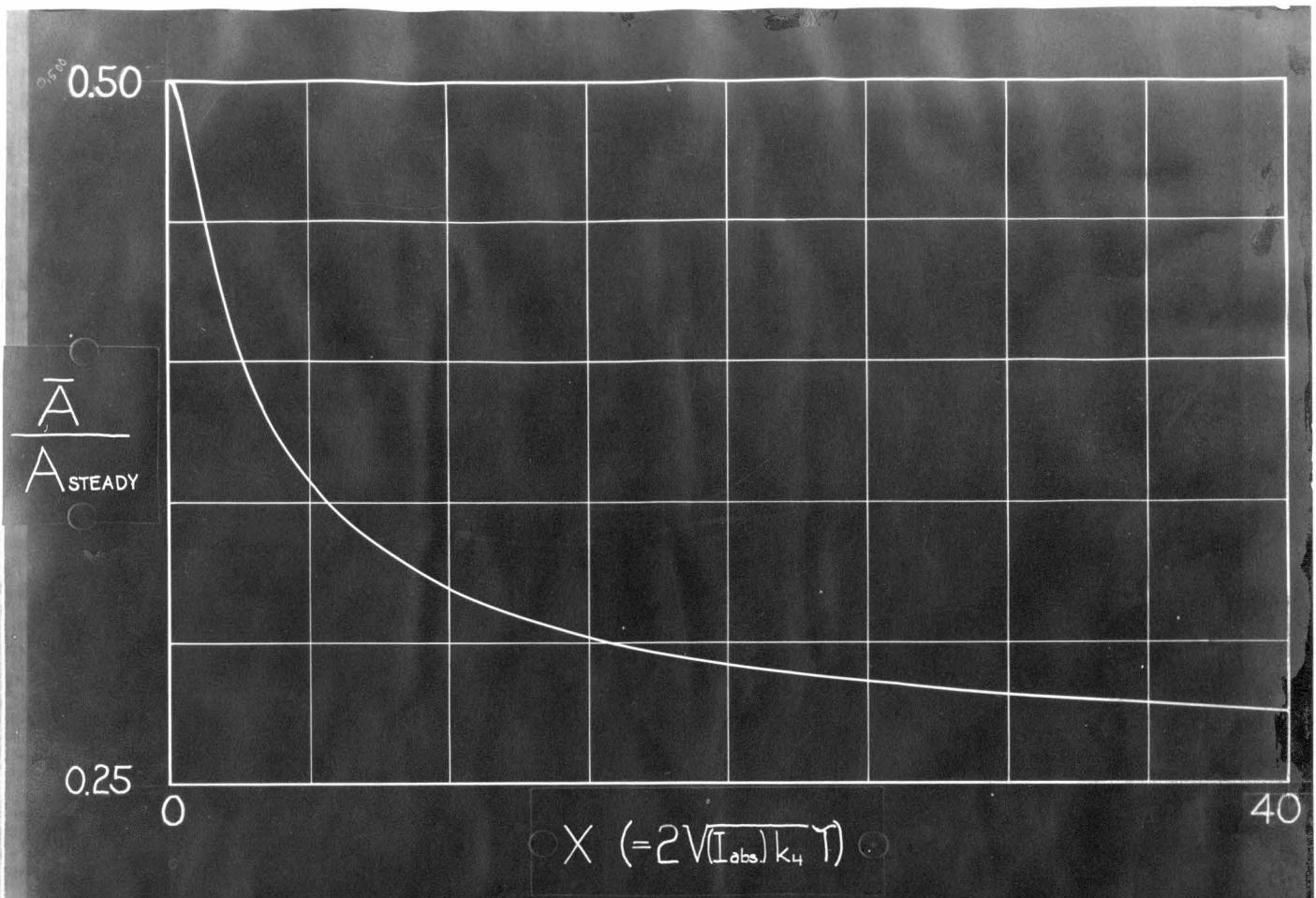
Figure 1

Figure 2

Figure 3