



Title	PHOTOCHEMICAL REACTIONS OF CHLOROFORM IN THE PRESENCE OF AQUEOUS SOLUTION
Author(s)	HORIUTI, Juro; KATAYAMA, Meiseki
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 6(1), 44-56
Issue Date	1958-07
Doc URL	http://hdl.handle.net/2115/24670
Type	bulletin (article)
File Information	6(1)_P44-56.pdf



[Instructions for use](#)

Photochemical Reactions of Chloroform in the Presence of Aqueous Solution

fications as follows. Calcium trichloroacetate was prepared by neutralizing "Guaranteed Reagent" of trichloroacetic acid in aqueous solution with solid "Extra Pure" calcium carbonate both from Kanto Chemical Co. Ltd., Tokyo; the solution was filtered, the filtrate evaporated up and the solid calcium trichloroacetate thus obtained dried in 10^{-5} mmHg vacuum at room temperature for a week until no stain of moisture was perceptible on the wall of a trap at liquid nitrogen temperature. The NaOD solution was formed by allowing distilled sodium metal to react in vacuum with 99.78% D₂O from Norsk Hydro-Elektrisk Co., Norway.

Deuteriochloroform liberated by warming the mixture of the above samples of calcium trichloroacetate and NaOD solution was condensed over granular calcium chloride, left standing overnight, decanted, alternately frozen in vacuum and molten in closed space several times for exhausting dissolved air, one third of the sample evaporated off in vacuum and the next one third collected for use by distillation in vacuum from -20°C to liquid nitrogen temperature.

The sample thus prepared was analyzed by means of HILGER's Model H 800 infrared spectrometer; the protochloroform content was 1.5% as follows from the result assuming the absence of absorption of deuteriochloroform at 3030 cm^{-1} band, i. e. the sample was at least 98.5% isotopically pure.

Ordinary chloroform was purified similarly as in the previous works¹⁾³⁾⁴⁾⁵⁾.

Radioactive chloride solution in heavy water was the mixture of distilled water, 99.78% D₂O mentioned above, aqueous solution of HCl^{*}) or NaCl^{**)} containing Cl³⁶ and a proper quantity of NaOH aq. or HCl aq. for adjusting pH. The deuterium content of the solution was determined by distilling it in vacuum, purifying the distillate by three times further vacuum distillations and observing the temperature at standstill of a standardized float in the purified distillate. The pH of the solution or "pH, Initial" in Table 1 was determined by titrating it with standard sulfuric acid or standard sodium hydroxide solution.

§ 2 Experimental Procedure

Two cc radioactive chloride solution in heavy water of known pH and known deuterium content, and 2 cc ordinary chloroform were sealed air-free in a quartz tube of 10 to 12 cc capacity as in the previous experiments¹⁾³⁾⁴⁾⁵⁾. The sealed tube thus prepared and its duplicate were shaken at 35°C , one under irradiation with a mercury lamp and the other screened from light by black paper.

The former was set horizontally inside a coaxial quartz jacket of 1.8 cm diameter parallel to the stem of the mercury lamp used in the previous work¹⁾ and was irradiated by condensing light of the mercury lamp on it by means of an aluminium reflector and

*) 1.67 N, 114 $\mu\text{c/gm}$ Cl, HCl³⁶ aq. or 2.16 N, 95 $\mu\text{c/gm}$ Cl, HCl³⁶ aq. supplied by Radioactive Centre, Amersham, England.

**) Recovered from radioactive chloride solutions used for similar experiments.

a simple quartz lens as shown in Fig. 1, while being shaken lengthwise over 2 cm range ca. 200 times p.m., and kept at 35°C by allowing thermostat water to flow through the 1.5 mm wide annular space under the jacket. The lens was of 3.8 cm diameter and 4.5 cm focal length for day light, which was set against the sealed tube surrounded by the jacket to focus the visible light at the opposite side of the object so as to condense ultraviolet rays inside the sealed tube. This optical arrangement was fixed common to every run of the present experiment. The above procedure of thermostating the sealed tube was preliminarily confirmed to be effective by means of a thermometer inserted together with chloroform and water in a tube of the same size, which was set in place of the sealed tube and shaken under irradiation quite similarly as the latter.

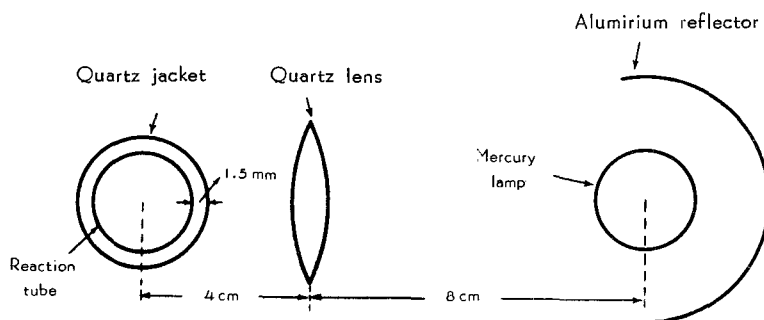


Fig. 1 Optical Arrangement.

The sealed tube under irradiation and that screened were opened respectively after a recorded time, chloroform inside was carefully pipetted out to separate it from aqueous solution, washed several times with distilled water and its one cc portion was observed for radioactivity. Putting now the latter back to the rest, the joint sample was dried, distilled in vacuum and its deuterium content determined by means of the infrared spectrometer mentioned above observing its optical density at 2256 cm^{-1} band, which was preliminarily standardized with known mixtures of 98.5% deuteriochloroform^{*)} and ordinary chloroform.

The reacted aqueous solution was titrated with standard sulfuric acid or standard sodium hydroxide solution for the final value of pH and analyzed for chloride ion concentration by the MOHR's method.

The rate V_d of chloroform decomposition per unit volume of the aqueous solution was given in accordance with the previous work⁴⁾ as

*) Cf. the last paragraph of "Deuteriochloroform" in §1; if the deuteriochloroform sample be richer than 98.5%, deuterium content of reacted chloroform samples must be slightly higher by the same factor. This, if at all, hardly affects the present conclusion in §4, since the relative deuterium content in reacted chloroform is just of significance there.

one third of the rate of increase of the chloride ion concentration, i. e.

$$V_a = \Delta[\text{Cl}^-]/3t, \quad (1)$$

where $\Delta[\text{Cl}^-]$ is the increment of chloride ion concentration $[\text{Cl}^-]$ during the time t of reaction.

The rate \bar{r} of chlorine exchange was expressed as

$$\bar{r} = \int_0^t \frac{r dt}{n^c n^s} / \int_0^t \frac{dt}{n^c n^s} = - \frac{n_0^c n_0^s}{\kappa_D v^s n t} \ln \left(1 - \frac{\alpha^c C_{1,t}^c v^c n}{\alpha^s C_{1,0}^s v^s n^c} \right), \quad (2. u)$$

which is the time mean of the rate r of the unidirectional transfer of chlorine from solution to chloroform per unit volume of the solution with the statistical weight $1/n^c n^s$, where n^c or n^s is the quantity of chlorine in chloroform or in solution, n the total quantity of chlorine, i. e. $n = n^c + n^s$ which is constant independent of time t , n_0^c or n_0^s the value of n^c or n^s at $t=0$, v^c or v^s the volume of chloroform or solution respectively taken constant, $C_{1,t}^c$ or $C_{1,0}^s$ the directly observed excess count over the background of 1 cc chloroform after the reaction or 1 cc aqueous solution before it, i. e. "Apparent Specific Radioactivity" shown in Table 1, and $\alpha^c = 4.39^{5)}$ or $\alpha^s = 3.72^{5)}$ the factor, which converts $C_{1,t}^c$ or $C_{1,0}^s$ into the respective count to be observed in the absence of selfabsorption under the particular condition of the present measurement, which is identical with that of the previous determination⁵⁾ of α^c and α^s . The κ_D in (2. u) is defined by the equation^{*})

$$\kappa_D = \frac{n_0^c n_0^s}{t} \int_0^t \frac{dt}{n^c n^s} = \frac{n_0^c n_0^s}{\dot{n}^c n t} \ln \frac{1 + \dot{n}^c t / n_0^c}{1 - \dot{n}^c t / n_0^s}, \quad (2. \kappa)$$

which tends to unity, by definition, as the rate $-\dot{n}^c$ of decrease of n^c or of increase of n^s , assumed constant independent of t , approaches zero.

Eq. (2) is derived from the kinetic equation^{**)}

$$d(n^c y^c) / dt = r v^s y^s - (r v^s - \dot{n}^c) y^c,$$

where y^s or y^c is the atomic fraction of radioactive chlorine in solution or in chloroform respectively and $r v^s$ or $r v^s - \dot{n}^c$ is the unidirectional rate of overall chlorine transfer from solution to chloroform or reverse respectively. This equation holds formally irrespective of the cause of the exchange reaction, thermal, photochemical or concerted, provided that radioactive and nonradioactive chlorines react with equal chance and in consequence that the respective unidirectional rate of radioactive chlorine transfer is given by the overall unidirectional rate $r v^s$ or $r v^s - \dot{n}^c$ times the appropriate atomic fraction y^s or y^c respectively. We have immediately from the above equation

*) Eq. (3.7. D. κ) of Ref. 5.

***) Eq. (3.1) of Ref. 5.

$$n^c dy^c / dt = v^s r (y^s - y^c)^{**}),$$

which is transformed into the form^{***)}

$$n^s n^c dy^c / dt = v^s r n^* (1 - y^c / y_\infty), \quad (3)$$

by introducing the notations

$$n^* \equiv n^s y^s + n^c y^c, \quad y_\infty \equiv n^* / n$$

for the total quantity of radioactive chlorine and its atomic fraction at interchange equilibrium.

Eq. (3) is integrated as

$$\ln(1 - y_i^c / y_\infty) = -n v^s \int_0^t r dt / n^c n^s,$$

observing that $y_0^c = 0$ at our experimental condition, where y_0^c or y_i^c is the value of y^c before or after the reaction respectively. Eq. (2) is arrived at by replacing y_i^c / y_∞ by $\alpha^c C_{1,i}^c v^c n / \alpha^s C_{1,0}^s v^s n^c$ in accordance with Eq. (3.8) of Ref. 5, and by dividing the resulting equation through by $\int_0^t dt / n^c n^s$.

In the previous work⁵⁾ r or r/n^s was evaluated by integrating (3) assuming it respectively constant during the reaction; since however r or r/n^s in the dark depends on pH⁵⁾, while pH shifts extensively under irradiation in the present experiments, Expression (2) of the chlorine exchange rate is preferred here to previous ones, which are only approximate in the present case. Actually n^c remains practically constant during the reaction, whereas n^s increases meanwhile by a factor 1.8~1.9 in runs 1 and 2 or by a few ten percent in other runs as inferred from the observed increment of chloride ion concentration in solution. It follows that the weighted time mean of (2) differs from the simple mean $1/t \cdot \int_0^t r dt$ in that the initial values of r are weighted more than the later ones by the above factor at most.

The similar time mean \bar{k}^s of the specific rate k^s of deuterium transfer from solution to chloroform was calculated from the observed results as

$$\bar{k}^s = \frac{1}{t} \int_0^t k^s dt = \frac{m^c m^s x_\infty^c}{v^s m^D t} \ln(1 - x_i^c / x_\infty^c), \quad (4. k)$$

where

$$x_\infty^c = m^D / (m^s / \gamma + m^c) \quad (4. x)$$

and

$$\gamma = k^s / k^c = 0.877^{6)}; \quad (4. r)$$

the specific rate k^s or k^c is the unidirectional rate of deuterium transfer

*) Eq. (3.2) of Ref. 5.

***) Eq. (3.4) of Ref. 5.

respectively from solution to chloroform or reverse per unit volume of solution reckoned respectively for unit deuterium atomic fraction in solution or in chloroform, m^c or m^s is the quantity of hydrogen in chloroform or in solution respectively participating the exchange reaction, m^D the total quantity of deuterium both in solution and chloroform, and x_i^c or x_∞^c the atomic fraction of deuterium in chloroform at time t or at the exchange equilibrium.

Eq. (4) is derived as follows. We have the kinetic equation

$$m^c \frac{dx^c}{dt} = v^s (k^s x^s - k^c x^c), \quad (5)$$

which holds irrespective of the concurrent decomposition⁶⁾ or of the irradiation, provided that the unidirectional rate of deuterium transfer from solution to chloroform or in the reverse direction is respectively proportional to the atomic fraction x^s in solution or that x^c in chloroform. Denoting the values of x^s and x^c , which satisfies (5) at $dx^c/dt=0$ by x_∞^s and x_∞^c respectively as

$$k^s x_\infty^s = k^c x_\infty^c$$

and the total amount of deuterium $m^s x^s + m^c x^c$ or $m^s x_\infty^s + m^c x_\infty^c$ by m^D as

$$m^s x^s + m^c x^c = m^s x_\infty^s + m^c x_\infty^c = m^D,$$

we have by eliminating k^c , x^s and x_∞^s from the above four equations

$$m^c m^s \frac{dx^c}{dt} = v^s k^s m^D (1 - x^c/x_\infty^c), \quad (6)$$

which is quite analogous to (3) of chlorine exchange. In the latter case the variation of n^s and n^c has been taken into account in terms of the statistical weight in the time mean of r . In the present case, however, m^c and m^s vary quite triflingly as follows from the magnitude $0.11 \text{ mol } \ell^{-1}$ at most of $\Delta[\text{Cl}^-]$ ^{*)}. We have (4.k) by integrating (6) admitting in consequence m^c and m^s practically constant and assuming that r , and hence x_∞^c according to (4.x), are practically unaffected by irradiation.

§ 3 Experimental Results

Experimental results are shown in Table 1. Each number of runs in the Table indicates a pair of contrasted experiments respectively under irradiation and in the dark as described in the foregoing section. The temperature was 35°C except for Run 11 conducted at 16°C. There

*) It follows from the value of $\Delta[\text{Cl}^-]$ that $-\Delta m^c = \Delta m^s = 0.11 \times 2 \times 10^{-3} \times 1/3 = 7 \times 10^{-5}$ mol according to (1) ignoring formic acid formed by decomposition to affect m^s ; this amount is negligible compared with $m^c = 2 \times 1.489/119.4 = 0.025$ mol or $m^s = 2 \times 2/18 = 0.22$ mol respectively. The Δm^s is even smaller, if formic acid excludes associated hydrogen from participating the exchange reaction. Cf. Appendix 2 of KANEKO and SATO (Ref. 6).

TABLE 1. Rates under Irradiation and in the Dark of Chloroform

No. of Runs	Time of Reaction min	Aqueous Chloride Solution, 2 cc					
		pH		Chloride Ion Concentration mol l ⁻¹		Apparent Specific Radioactivity, Initial, C _{1,0} ^s ct min ⁻¹ cc ⁻¹	
		Initial	Final	Initial	Final		
1 c)	irrad.	65	13.62±0.00	13.59±0.00	0.122±0.002	0.230±0.002	19000 ± 50
	dark	"	13.63 "	13.56 "	0.115 "	" "	17970 "
2 c)	irrad.	360	12.94 "	12.67 "	0.128 "	0.234 "	21040 "
	dark	"	" "	" "	" "	0.233 "	" "
3 b)	irrad.	720	12.23 "	11.55±0.02	0.110 "	0.136 "	19740 "
	dark	"	" "	11.74±0.01	" "	0.131 "	" "
4 b)	irrad.	720	12.23 "	11.55±0.02	0.110 "	0.135 "	19740 "
	dark	"	" "	11.74±0.01	" "	0.129 "	" "
5 a)	irrad.	240	12.15 "	11.81 "	0.090 "	0.102 "	17840 "
	dark	480	" "	11.91 "	" "	0.099 "	" "
6 a)	irrad.	720	12.15 "	2.75±0.02	0.090 "	0.121 "	17840 "
	dark	"	" "	11.81±0.01	" "	0.106 "	" "
7 a)	irrad.	1440	12.15 "	2.08 "	0.090 "	0.136 "	17840 "
	dark	"	" "	11.66 "	" "	0.110 "	" "
8 a)	irrad.	1440	11.59±0.01	1.52±0.00	0.139 "	0.180 "	29110±210
	dark	5900	" "	11.18±0.03	" "	0.140 "	" "
9 c)	irrad.	1440	2.92±0.00	1.53±0.00	0.109 "	0.145 "	16300 ± 50
	dark	"	" "	2.92 "	" "	0.109 "	" "
10 b)	irrad.	720	1.28 "	1.18 "	0.146 "	0.157 "	23420 "
	dark	"	" "	1.28 "	" "	0.150 "	" "
11 a)*)	irrad.	1440	11.59±0.01	1.88 "	0.139 "	0.166 "	29110±210
	dark	10565	" "	11.47±0.02	" "	0.139 "	" "

*): at 16°C.

a): 1.67 N, 114 μc/gm Cl, HCl³⁶ aq. from Radioactive Centre, Amersham, England, used for the preparation of "Aqueous Chloride Solution".

b): 2.16 N, 95 μc/gm Cl, HCl³⁶ aq. from the same source as of a), used.

c): NaCl³⁶ aq. recovered from wastes of the similar previous experiments, used.

Photochemical Reactions of Chloroform in the Presence of Aqueous Solution

Decomposition (\bar{V}_d), Chlorine Exchange (\bar{r}), and Hydrogen Exchange (\bar{k}^s), 35°C

Deuterium Atomic Fraction, Initial, x_0^s %	Chloroform, 2cc		Rates		
	Apparent Specific Radioactivity, Final, $C_{1,t}^s$ ct min ⁻¹ cc ⁻¹	Deuterium Atomic Fraction, Final, x_t^s %	Decomposition $\bar{V}_d \times 10^6$ mol l ⁻¹ min ⁻¹	Chlorine Exchange $\bar{r} \times 10^6$ mol l ⁻¹ min ⁻¹	Hydrogen Exchange $\bar{k}^s \times 10^2$ mol l ⁻¹ min ⁻¹
•	465±5	•	558 ±15	98.7±4.2	•
•	476 "	•	592 "	113.5±5.8	•
•	612 "	•	98.2±2.6	21.3±0.9	•
•	607 "	•	97.6 "	21.1 "	•
27.8±0.3	93 "	19.3±0.2	12.1±1.3	0.97±0.06	2.65±0.12
" "	132 "	22.0±0.3	9.5 "	1.34 "	4.75±0.59
27.8 "	84 "	1.83±0.2	11.4 "	0.87 "	2.26±0.09
" "	120 "	22.0±0.3	8.6 "	1.20 "	4.75±0.59
22.5 "	26 "	6.0±0.1	16.4±3.9	0.69±0.13	1.68±0.04
" "	63 "	13.0±0.2	6.4±2.0	0.83±0.07	2.61±0.10
22.5 "	59 "	12.0±0.2	14.2±1.3	0.59±0.05	1.50±0.05
" "	96 "	14.5 "	7.3 "	0.87±0.06	2.18±0.10
22.5 "	89 "	11.5 "	10.6±0.7	0.50±0.03	0.69±0.02
" "	107 "	22.5±0.3	4.5 "	0.50 "	equilibrium
22.5±0.2	213 "	<0.3	9.5 "	0.95 "	<0.03
" "	31 "	5.8±0.1	<0.2	0.03±0.01	0.07±0.01
30.0±0.3	314 "	<0.3	8.3±0.7	2.08±0.07	<0.03
" "	<5	"	<0.7	<0.03	"
28.0 "	52±5	<0.3	5.1±1.3	0.53±0.05	<0.05
" "	13 "	"	1.8 "	0.13 "	"
22.5±0.2	176 "	"	6.4±0.7	0.74±0.03	<0.03
" "	<5	"	<0.1	<0.004	<0.004

are given probable errors in the Table as derived from those of direct observations. Those rates are recorded simply as less than the positive of the appropriate probable errors which came out by calculation to lie within them.

We see from runs 1 and 2 that the irradiation affects the rates of decomposition as well as of chlorine exchange almost imperceptibly at these high pH; the simultaneous hydrogen exchange has not been observed because of the preliminary result not reported here that the exchange practically attained equilibrium under the appropriate condition.

At lower pH of runs from No. 3 to No. 7, the decomposition is perceptibly accelerated by irradiation, whereas the rates of simultaneous chlorine and hydrogen exchange are rather decreased than increased by irradiation. Chlorine exchange as well as decomposition is, however, noticeably accelerated by irradiation at still lower pH, while hydrogen exchange is hardly affected even there. Markedly accelerated rates of chlorine exchange and of decomposition remain moreover, as seen from the Table, respectively of the same order of magnitude independent of pH or, perhaps tolerably constant within the expected fluctuation of the effective intensity of irradiation.

The acceleration of decomposition by irradiation is accompanied by a pronounced pH-depression, as it should be, as seen from Table 1. Three times as much time is thus required for the dark run of No. 6 to give rise to the same pH-decrease from 12.15 to 11.81 as that for the irradiated run of No. 5, while the same time of reaction for the irradiated run of No. 6 causes the decrease of pH from 12.15 as much as down to 2.75.

The result of run 11 conducted at 16°C corresponds almost to that of run 8 at 35°C with the common initial pH.

§ 4 Discussion of Results

The present experimental results are at variance with the previous conclusion¹⁾ that the irradiation increases the rates of chlorine exchange and hydrogen exchange by the same factor, which was based on the assumption A) that the photochemical reaction follows the same sequence of elementary steps as the thermal one and B) that its first step $\text{CHCl}_3 \rightarrow \text{H}^+ + \text{CCl}_3^-$ of the sequence¹⁾ is photochemically accelerated. Either or both of A) and B) must in consequence be negatived. It is

shown however that the present experimental results is not fitted in with by any other step of the sequence assumed to be photochemically accelerated in place of the above first one, in so far as A) is reserved as valid. It is hence concluded that the photochemical reaction must follow some other sequence different from that of the thermal one.

We now postulate, amplifying the above conclusion, that photochemical and thermal reactions proceed concurrently independent of each other, the rates both of photochemical decomposition and of such chlorine exchange are independent of pH, and the hydrogen exchange occurs only thermally, on which basis the present experimental results are accounted for as follows.

The observed rate of decomposition under irradiation at lower pH should now be ascribed practically exclusively to the photochemical reaction, since the rate in the dark is negligibly small in the same pH-range as compared with that under irradiation. This rate under irradiation being yet considerably smaller than the rate at higher pH observed either under irradiation or in the dark, the photochemical contribution must be negligible against the thermal one at the higher pH, in accord with the apparent inefficacy of irradiation there.

The chlorine exchange under irradiation at lower pH (runs 8, 9, 10 and 11) may quite similarly be attributed practically exclusively to the photochemical reaction, whereas that at higher pH either under irradiation or in the dark to the thermal one, because of the similar situation that \bar{r} of exchange in the dark is negligibly small as compared with that under irradiation at lower pH (Table 1), while the latter is even by far smaller than \bar{r} at higher pH either in the dark or under irradiation (Table 1).

The decrease of the chlorine exchange rate by irradiation at the intermediate pH (runs from 3 to 7) is now explained as follows with due regard to its large thermal rate at higher pH, which decreases with decreasing pH down to pH *ca.* 6, beyond which it remains constant independent of pH^{5)*)}. The r of chlorine exchange may be written as the sum of the thermal contribution r_T and the photochemical one r_P in accordance with the above postulate. The \bar{r} is now the sum of the average \bar{r}_T of r_T and constant r_P , i.e.

$$\bar{r} = \bar{r}_T + r_P$$

in conformity with (2.u).

*) This dependence observed at 100°C is assumed qualitatively valid here at 35°C.

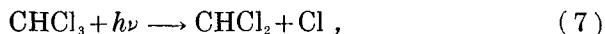
Let a run begin at higher pH, where r_T is considerably large in comparison with its constant value at lower pH and the pH-range be extended downwards by irradiation beyond that in the dark as is actually the case with all runs in Table 1 except Nos. 1 and 2. The average \bar{r}_T of r_T is reduced by irradiation because of the two causes, i.e. the smaller time spent at higher pH where r_T is larger and the associated extension of the average to smaller r_T at lower pH. As a run begins at lower pH, the decrease of \bar{r}_T due to the irradiation diminishes along with the decrease of initial r_T , reducing practically to nil for sufficiently low pH in the beginning. The increase $\Delta\bar{r}$ of \bar{r} by irradiation is now given, on account of the absence of r_p in the dark, as

$$\Delta\bar{r} = \Delta\bar{r}_T + r_p,$$

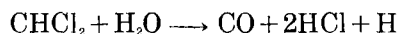
where r_p is positive, while $\Delta\bar{r}_T$ is negative tending to zero as the initial pH decreases as deduced above. This explains the observed photoeffect $\Delta\bar{r}$ on \bar{r} in Table 1, that it is appreciably negative, when the initial pH is high enough and the final pH is extended lower by irradiation beyond that in the dark, whereas it turns positive, as the initial pH lowers.

The photoeffect $\Delta\bar{k}^s$ on the hydrogen exchange consists exclusively of the thermal part $\Delta\bar{k}_T^s$ which corresponds to $\Delta\bar{r}_T$, because of the postulated absence of the photochemical exchange. Since however k_T^s varies with pH similarly as r_T as observed by KANEKO and SATO⁶⁾, it follows likewise that $\Delta\bar{k}^s$ is negative for runs beginning with high pH, tending to zero with decreasing initial pH but never turns positive. This is in accord with the experimental results given in Table 1.

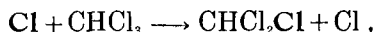
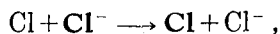
In accordance with the above postulate so far experimentally verified, the mechanism of photochemical decomposition and the chlorine exchange might be advanced that the photochemical primary process consists in the step



followed by thermal steps resulting in the decomposition of one of the products, CHCl_2 , i. e.,



and by further thermal steps to do with the other product, i. e. atomic chlorine Cl, as

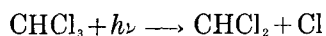


giving rise to the exchange of chlorine Cl from chloroform for that Cl from solution. The photochemical primary process (7) is that suggested by HENRICI⁷⁾ for the photochemical dissociation of chloroform vapour. Atomic hydrogen and chlorine will recombine to form molecular hydrogen, chlorine and hydrogen chloride^{*)}, leaving only a fraction of atomic chlorine originally formed to accomplish the exchange reaction. It follows then that the photochemical \bar{r} is but a fraction of the photochemical V_d as actually observed at lower pH.

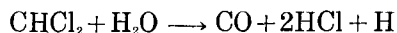
Summary

Photochemical effects of irradiation upon the decomposition, the chlorine exchange and the hydrogen exchange of chloroform coexistent with the aqueous solution of pH from 1.2 to 13.6 containing deuterium and radioactive chlorine were simultaneously observed at 35°C with a mercury lamp of the spectral range down to 2100 Å. It was thus found that both the decomposition and the chlorine exchange were markedly accelerated at lower pH but not perceptibly at higher pH, that the hydrogen exchange was not accelerated throughout, that the chlorine and the hydrogen exchange were even retarded over the intermediate pH-range and that the rate of photochemical chlorine exchange was a small fraction of that of photochemical decomposition at lower pH.

These experimental results were accounted for on the basis of the pH-dependence of the above three reactions in the dark⁴⁾⁵⁾⁶⁾ and of the proposed mechanism of the photochemical decomposition and chlorine exchange, which consists of the photochemical primary process

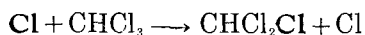
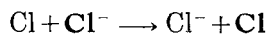


and the secondary processes resulting in the decomposition



*) Eq. (1) holds exactly, provided that hydrogen and chlorine combine with each other exclusively to form hydrogen chloride under irradiation. Otherwise, (1) should yield more or less too low a value of V_d .

on the one hand and in the chlorine exchange



(Cl: chlorine atom from chloride ion in the aqueous solution) on the other hand.

Infrared observations in the present work has been kindly conducted by Assist. Prof. S. MATSUSHITA of this University to whom the present authors' best thanks are due. They wish also to thank Prof. T. HORI of this University and Prof. M. KOIZUMI of Tohoku University for their kind helps and valuable advices, and moreover to acknowledge the grant in Aid for Fundamental Scientific Research of the Ministry of Education.

References

- 1) J. HORIUTI and K. TANABE, Proc. Japan Acad. **29**, 254 (1953).
- 2) M. H. EARING and J. B. CLOKE, J. Am. Chem. Soc. **73**, 769 (1951).
- 3) J. HORIUTI and K. TANABE, Proc. Japan Acad. **27**, 404 (1951); *ibid.* **28**, 130 (1952).
- 4) J. HORIUTI, K. TANABE and K. TANAKA, this Journal **3**, 147 (1955).
- 5) J. HORIUTI, K. TANABE and K. TANAKA, this Journal **3**, 119 (1955).
- 6) Y. KANEKO and Y. SATO, this Journal **6**, 28 (1958).
- 7) A. HENRICI, Z. Physik **77**, 35 (1932).