Title	CHLORINE EXCHANGE REACTION BETWEEN CHLOROFORM AND AQUEOUS CHLORIDE SOLUTION
Author(s)	HORIUTI, Juro; TANABE, Kozo; TANAKA, Kazunori
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 3(3), 119-146
Issue Date	1955-03
Doc URL	https://hdl.handle.net/2115/24632
Type	departmental bulletin paper
File Information	3(3)_P119-146.pdf

CHLORINE EXCHANGE REACTION BETWEEN CHLOROFORM AND AQUEOUS CHLORIDE SOLUTION

By

Juro HORIUTI, Kozo TANABE and Kazunori TANAKA

(Received March 10, 1955)

Introduction

It has been found by means of Cl^{36} as a tracer that chloroform exchanges chlorine at room temperature with alkaline chloride solution either thermally[1),3)] or photochemically[4)] but not perceptibly with acidic solution in either way; carbon tetrachloride exchanged thermally neither with alkaline nor with acidic solution, whereas photochemically it did with acidic solution but not with alkaline solution.[2),4)]

The chlorine exchange has now been investigated in detail at 100°C with special reference to the effect of chloride ion concentration, of pH and of wall area on the rate. The experimental result has been discussed incorporated with that of decomposition[5)] and of hydrogen exchange[6)] of chloroform under the similar condition, and its mechanism deduced as described in what follows.

§ 1. Experimental Procedure

One and half cc or 2 cc chloroform was sealed air-free together with 1 or 2 cc aqueous radioactive chloride solution of known concentration and of known pH, in a quartz tube of 23～28 cc capacity similarly as in the previous works[1),4)] and shaken briskly at 100°C for a recorded time; the quartz tube was now opened, 1 cc chloroform carefully pipetted out, its radioactivity determined as in the previous work[1)] by putting 1 cc sample in a definite stainless steel tray fitted to a definite G-M counter*), then washed by distilled water and the washing measured for the radioactivity for control of the contamination of the radioactive solution at the pipetting; if found radioactive the

---

*) Model 16, Supplied by the Scientific Research Institute, Tokyo.

radioactivity measurement of chloroform and subsequent procedures were started anew.

The radioactivity of the solution before the contact, i. e., before the above treatment, was determined just similarly as that of chloroform after contact using the same definite apparatus. The specific radioativity (radioactivity in the absence of self-absorption) of the solution as well as of chloroform was obtained by multiplying the apparent radioactivity of the excess count over the background count observed directly as above by the respective conversion factor, particular to the above procedure of measurement; the factor was determined as described below in § 2.

The radioactive chloride solution was (i) a simple dilution of the preparation of the US Atomic Energy Comission with the specification "1.46 N HCl of 0.23 mc/gm" or the latter admixed with H_2SO_4 aq. or NaOH aq. for approximately adjusting pH or, (ii), the same dilution saturated with one of solid hydroxides of magnesium, calcium, barium and silver for retarding the pH-decrease due to the decomposition product.

The pH of solution (i) was measured at room temperature before and after contact by means of Beckman pH-meter*) or of pH test paper; extremely strong alkaline solution (run 8 of Table 3) was titrated with standard oxalic acid solution instead of being measured for pH as above. The pH at 100°C of solution (i), except that conducted in extremely high ionic strength (runs 8, 10, 18 and 19 of Table 3) was calculated from that measured at room temperature allowing for ionic interaction according to the limiting law as detailed in the subsequent paper[5]) in connection with the decomposition measurement.

The pH of solution of high ionic strength was dealt with as follows, because of expected unreliability of the limiting law. The low pH around 1 (runs 10, 18 and 19 of Table 3) observed at room temperature which has necessarily a high ionic strength was simply identified with that at 100°C on the ground of the experimental fact that low pH of aqueous strong acid has very small temperature coefficient. The pH of the extremely strong alkaline solution (run 8 of Table 3) was given conventionally as a mere transcription of the titrated concentration of hydroxide ion on the basis of known dissociation constant K_h of water either at room temperature or at 100°C taking activity coefficients

---

*) BECKMAN Glass Electrode pH meter (Model G), BECKMAN Instruments Inc.

involved respectively unity.

The pH at 100°C of (ii) before contact was calculated as described in the subsequent paper[5] allowing for the ionic interaction from known solubilities of solid hydroxides given below.

Solubilities*) of Hydroxides
gm/100 cc. at 100°C

$Mg(OH)_2$	4.2×10^{-4}	
$Ca(OH)_2$	6.9×10^{-2}	
$AgOH$	3.1×10^{-3}	(extrapolated)

The pH of solution (ii) after contact and the amount of chloride ion liberated were calculated from the above solubility data, contact time and the decomposition rate observed in the experiment of the subsequent paper[5].**)

The exchange rate of chlorine at known pH of the solution at 100°C was now calculated from the above determination of the specific activity allowing for the simultaneous decomposition as stated in § 3.

§ 2. Specific Radioactivity

It may readily be shown, neglecting the back-scattering, that the apparent radioactivity C or the directly observed count minus the background count of a sample in a definite tray***) fitted to a definite G–M counter****), varies with its volume v as,

---

*) A. SEIDELL: Solubilities of Inorganic and Metal Organic Compounds. (1940) New York., D. Van NOSTRAND Co. Inc.

**) The increment $\varDelta[Cl^-]$ of chloride ion concentration in solution was calculated as function of pH from known solubility of solid hydroxide as detailed in the subsequent paper; the decomposition rate $[\dot{Cl}^-]\equiv d\varDelta[Cl^-]/dt$ being determined as function of pH there, we have the relation between $d\varDelta[Cl^-]/dt$ and $\varDelta[Cl^-]$, i. e., $\frac{d\varDelta[Cl^-]}{dt}=F(\varDelta[Cl^-])$ or by integration, $\int_0^t \frac{d\varDelta[Cl^-]}{F(\varDelta[Cl^-])}=t$

Plotting now $1/F(\varDelta[Cl^-])$ against $\varDelta[Cl^-]$ and adjusting the area under the curve to the observed time of contact, we obtain $\varDelta[Cl^-]$ and appropriate pH.

These values are however crude, inasmuch as in the above calculation of $\varDelta[Cl^-]$ as function of pH, the activity coefficients involved were equated respectively to unity conventionally, because of the unreliability mentioned in the text of the method of exacting activity coefficients at high ionic strength due to the accumulation of the bivalent metallic ion of solid hydroxides along with the progress of decomposition as turned out by the calculation.

***) Circular tray of 2.5 cm diameter and 0.6 cm height.

****) Cf. foot-note on page 119.

$$\log\left(1-\alpha\frac{C}{C_l}\right) = -\alpha v^{*)} \qquad (2.1)$$

where,

$$\alpha = -\frac{1}{I}\frac{dI}{dl}$$

is the rate of decrease of intensity I of radiation with increase of volume l of the horizontal layer of the liquid sample in the tray traversed by it and C_l the specific radioactivity, which would be observed under the specified condition in the absence of self-absorption.

Tables 1 and 2 show C observed at different v, constants α and C_l fitted to the latter in accordance with (2.1), C calculated by (2.1) with these constants and the factor a which converts apparent specific activity C_1, i.e., C at $v=1$ into C_l.

TABLE 1 Self-Absorption of Chloroform

Sample:—Radioactive chloroform prepared by exchange reaction.

$\alpha = 4.316$ $\quad C_l = 6187$ $\quad a = \frac{C_l}{C_1} = 4.39$

v cc.	0.1	0.2	0.3	0.5	0.8	1.1
$C_{\text{obs.}}$ ct/min.	460	798	1080	1300	1370	1400
$C_{\text{calc.}}$ ct/min.	502	829	1040	1268	1387	1420

TABLE 2 Self-Absorption of Aqueous Chloride Solution

Sample:—Dilution of aqueous hydrogen chloride preparation supplied and specified as 1.46 N HCl of 0.23 mc/gm by the U. S. Atomic Energy Commission.

$\alpha = 3.26$ $\quad C_l = 5180$ $\quad a = \frac{C_l}{C_1} = 3.72$

v cc.	0.1	0.2	0.3	0.6	0.9	1.0
$C_{\text{obs.}}$ ct/min.	400	720	970	1306	1366	1372
$C_{\text{calc.}}$ ct/min.	434	736	946	1267	1367	1392

---

*) Integrating $\alpha = -\frac{1}{I}\frac{dI}{dl}$, we have $\frac{I}{I_0} = e^{-\alpha l}$, where I_0 is the contribution I to the observed radioactivity at $l=0$. Eq. (2.1) in the text is obtained by substituting I_0 in the above expression by $C_l dl$ and equating to C the integral of I thus expressed from 0 to v.

§ 3. Exchange Rate Expression

The chlorine exchange reaction proceeds, as reported previously[1], between chloroform and aqueous chloride solution in contact with each other accompanied by the decomposition of chloroform.

Chlorine should hence be transferred forwards from solution to chloroform and backwards, the balance of the respective rates being the net rate $\dot{n}^C$ of chlorine increase in chloroform, which is practically negative in accordance with the observed decomposition. Let the forward rate reckoned to unit volume of solution be r: the total forward rate is rv^S, the appropriate backward one $rv^S-\dot{n}^C$ and the rate of transfer of radioactive chlorine in particular from solution to chloroform $rv^Sx^S-(rv^S-\dot{n}^C)\,x^C$, where x^S or x^C is the atomic fraction of radioactive chlorine in solution or in chloroform respectively. The forward rate r will be called the exchange rate in what follows.[*]

The latter rate of isotopic transfer $rv^Sx^S-(rv^S-\dot{n}^C)x^C$ being alternatively expressed by $d\,(n^Cx^C)/dt$ where n^C is the amount of chlorine in chloroform and t the time elapsed during the contact, we have,

$$\frac{d(n^Cx^C)}{dt} = rv^Sx^S-(rv^S-\dot{n}^C)\,x^C \tag{3.1}$$

or

$$n^C\dot{x}^C = rv^S(x^S-x^C) \tag{3.2}$$

Defining the total amount n of chlorine present in the reaction vessel and that n^* of radioactive chlorine respectively as,

$$n \equiv n^C+n^S \tag{3.3.a}$$

$$n^* \equiv n^Cx^C+n^Sx^S \tag{3.3.b}$$

where n^S is the quantity of chloride ion in the solution, we have from (3.2) and (3.3),[**]

$$n^Cn^S\frac{dx^C}{dt} = rv^S(n^*-nx^C) \tag{3.4}$$

---

[*] The exchange rate thus defined is of course identical particularly with the forward and backward rates balanced with each other in the case of simple exchange reaction when each participant is neither consumed nor created.

[**] Eq. (3.3) stands for (3.3 a) and (3.3. b). This manner of reference will be followed below throughout.

Along with the progress of decomposition, n^C decreases, whereas n^S increases, both at the same rate $-\dot{n}^C$. If the chlorine exchange be controlled for instance by the step,

$$CCl_2 + Cl^- \longrightarrow CCl_3^- \qquad (3.5.D)$$

followed by another,

$$CCl_3^- + H^+ \longrightarrow CHCl_3 \qquad (3.5.H)$$

both in equilibrium, r or the rate of (3.5.D) is constant independent of the activity of chloride ion at constant pH, inasmuch as the same is true with the activity of CCl_3^- and hence with the rate of the reversal of (3.5.D), which equals r because of the equilibrium.

If on the other hand the exchange be controlled by the step,

$$Cl^- + CCl_3^- \longrightarrow ClCCl_2^- + Cl^- \qquad (3.5.S)$$

instead of by (3.5.D) but with (3.5.H) still in equilibrium, r must be proportional to the activity of chloride ion or, identifying the latter with concentration $[Cl^-]=n^S/v^S$, $r/[Cl^-]$ must be constant. Assuming

$$u_D \equiv r \quad \text{or} \quad u_S \equiv r/[Cl^-] \qquad (3.6.D),\ (3.6.S)$$

alternatively constant indendent of $[Cl^-]$ or of n^S, (3.4) may be integrated as,

$$u_D = -\log(1-x^C/x_\infty)\Big/v^S n\int_0^t \frac{dt}{n^C n^S}, \quad r \quad \text{const.}$$

$$u_S = -\log(1-x^C/x_\infty)\Big/n\int_0^t \frac{dt}{n^C}, \quad r/[Cl^-] \quad \text{const.}$$

where $x_\infty = n^*/n$ is x^C at $\dot{x}^C=0$ according to (3.4) or x^C-value attained when radioactive chlorine atoms were distributed evenly between chloroform and solution.

Carrying out the integral in the denominator expressing n^C and n^S as,

$$n^C = n_0^C + \dot{n}^C t, \qquad n^S = n_0^S - \dot{n}^C t$$

assuming $\dot{n}^C$ constant, we have,

$$u_D = -\frac{n_0^C n_0^S}{\kappa_D v^S n t}\log(1-x^C/x_\infty) \qquad (3.7.D.r)$$

where,

$$\kappa_D = \log \frac{1+\dot{n}^C t/n_0^C}{1-\dot{n}^C t/n_0^S} \Big/ \dot{n}^C \left(\frac{1}{n_0^C} + \frac{1}{n_0^S} \right) t \qquad (3.7.D.\kappa)$$

or

$$u_S = -\frac{n_0^C}{\kappa_S n t} \log (1 - x^C/x_\infty) \qquad (3.7.S.r)$$

where,

$$\kappa_S = n_0^C \log (1 + \dot{n}^C t/n_0^C)/\dot{n}^C t \qquad (3.7.S.\kappa)$$

Both κ_D and κ_S reduce to unity, as readily be seen, as $\dot{n}^C$ approaches zero. The x^C/x_∞ in $(3.7.D.r)$ or in $(3.7.S.r)$ may be expressed as,

$$x^C / x_\infty = \frac{a^C C_{1,t}^C v^C n}{a^S C_{1,0}^S v^S n^C} \qquad (3.8)$$

where $C_{1,t}^C$ or $C_{1,0}^S$ is C_1 of chloroform at t or of solution at $t=0$ respectively, and a^C or a^S the appropriate conversion factor a given in Tables 1 and 2, hence $a^C C_{1,t}^C v^C$ or $a^S C_{1,0}^S v^S$ respectively is proportional to the number of radioactive chlorine atoms present in chloroform at time t or the total number present in the reaction vessel.

Eqs. (3.7) allows us to work out u_D or u_S from the observation of $C_{1,t}^C$, $C_{1,0}^S$ etc.

For small $|\dot{n}^C t/n_0{}^C|$ or $|\dot{n}^C t/n_0{}^S|$ compared with unity, κ_D or κ_S may be expanded as,

$$\kappa_D = 1 + \frac{1}{2} \left(\frac{\dot{n}^C t}{n_0{}^S} - \frac{\dot{n}^C t}{n_0{}^C} \right) + R_D \qquad (3.9.D)$$

$$\kappa_S = 1 - \frac{\dot{n}^C t}{2 n_0{}^C} + R_S \qquad (3.9.S)$$

where R_D or R_S is the remainder, i. e.

$$R_D = \left\{ \frac{(\dot{n}^C t/n_0{}^C)^3}{(1+\theta_D \dot{n}^C t/n_0{}^C)^3} + \frac{(\dot{n}^C t/n_0{}^S)^3}{(1-\theta_D \dot{n}^C t/n_0{}^S)^3} \right\} \Big/ 3 \left(\frac{\dot{n}^C t}{n_0{}^C} + \frac{\dot{n}^C t}{n_0{}^S} \right)$$

and

$$R_S = \frac{(\dot{n}^C t/n_0{}^C)^2}{3(1+\theta_S \dot{n}^C t/n_0{}^C)^3}$$

with positive proper fraction θ_D or θ_S. It may readily be shown, noting that $\dot{n}^C$ is the only negative quantity involved in the above two expressions, that,

$$0 < R_D < \frac{(\dot{n}^C t)^2}{3} \left(\frac{1}{(n^C)^3} + \frac{1}{(n_0{}^S)^3} \right) \Big/ \left(\frac{1}{n_0{}^C} + \frac{1}{n_0{}^S} \right) \qquad (3.10.D)$$

$$0 < R_S < \frac{(\dot{n}^C t)^2}{3} \frac{n_0{}^C}{(n^C)^3} \qquad (3.10.S)$$

which discriminate whether the first two terms respectively of $(3.9.D)$ or $(3.9.S)$ sufficiently reproduce κ_D or κ_S; (3.9) was used for numerical calculation for small $|\dot{n}^S t/n_0{}^C|$ or $|\dot{n}^C t/n_0{}^S|$ compared with unity.

TABLE 3 Exchange of Chlorine Labelled by Cl^{36}

No. of Runs	Date	Time of Contact min.	Aqueous HCl*					
			Radioactivity before Contact		pH (100°C)		Qt. Cl^- ion	
			ct/min. cc	Background Count ct/min.	before contact	after contact	before n_0^S m mol	after n^S m mol
1	Dec. 1, 1952	6825	30800	34	1.35 (1.31)	1.27 (1.23)	0.146	0.169
2	〃	20	30800	34	10.97 (12.80)	6.01 (6.35)	——	——
3	〃	20	12320	34	7.29 (9.30)	5.57 (5.57)	——	——
4	〃	1970	13840	34	6.00 (6.35)	2.68 (2.68)	0.066	0.070
5	Dec. 16, 1952	54	13920	34	10.49	9.62	0.066	3.47
6	〃	536	13920	34	——	(6.7)	——	——
7	〃	2120	15400	34	8.43	2.2 (2.2)	——	——
8	Jan. 28, 1953	1	17410	34	12.74 (14.54)	12.15 (13.95)	0.050	1.805
9	Feb. 21, 1953	6220	20960	34	3.6 (3.6)	1.2~1.8 (1.2~1.8)	0.100	0.121
10	Mar. 5, 1953	6130	24000	33	0.1 (0.1)	0.1 (0.1)	0.115	0.136
11	〃	6130	27200	33	1.5 (1.3)	1.4 (1.2)	1.06	1.081
12	Feb. 16, 1954	1.33	11410	35	10.49	10.15	0.054	0.35
13	〃	10	11410	35	10.49	9.84	0.054	1.21
14	〃	2010	11410	35	8.47	6.97	0.054	0.354
15	〃	2010	11410	35	1.6 (1.5)	1.4 (1.3)	1.71	1.72
16	Feb. 19, 1954	1.0	8800	34	11.07 (12.88)	10.58 (12.40)	0.023	0.439
17	〃	1.0	8800	34	11.07 (12.88)	10.58 (12.40)	0.023	0.439
18	Feb. 20, 1955	3050	21840	36	(1.3)	(1.2)	8.104	8.114
19	Feb. 16, 1955	2000	21840	36	(1.3)	(1.2)	8.104	8.111

between Chloroform and Aqueous Chloride at 100°C.

		Chloroform					Rates	
		Radioactivity after Contact			Qt. Cl-Atom			
Volume v^S cc	Additions	ct/min. cc	Background Count ct/min.	Volume v^C cc	before n_0^C m mol	Rate of Decrease $-\dot{n}^C/v^S$ mol/l. min.	$\log_{10} u_D$ mol/l. min.	$\log_{10} u_S$ min.$^{-1}$
2	None	213	36	1.5	56.1	1.686×10^{-6}	$\bar{8}.765$	$\bar{7}.874$
2	NaOH	1440	32	1.5	56.1	1.686×10^{-6}	——	——
2	NaOH	35	34	1.5	56.1	——	——	——
2	NaOH	52	34	1.5	56.1	1.06×10^{-6}	$\bar{8}.296$	$\bar{7}.770$
2	Sat. Ca $(OH)_2$	4688	34	1.5	56.1	3.15×10^{-2}	$\bar{3}.257$	$\bar{3}.830$
2	Sat. Ba $(OH)_2$	1808	34	1.5	56.1	——	——	——
2	Sat. AgOH	299	34	1.5	56.1	——	——	——
1.2	NaOH	3760	35	1.8	67.3	15.0	0.186	$\bar{1}.809$
2	H_2SO_4	147	37	1.5	56.1	1.686×10^{-6}	$\bar{8}.600$	$\bar{7}.876$
2	H_2SO_4	118	36	1.5	56.1	1.686×10^{-6}	$\bar{8}.473$	$\bar{7}.695$
2	NaCl	125	34	1.5	56.1	1.686×10^{-6}	$\bar{7}.419$	$\bar{7}.685$
2	Sat. Ca $(OH)_2$	432	34	2.0	74.8	1.13×10^{-1}	$\bar{3}.254$	$\bar{2}$ 503
2	Sat. Ca $(OH)_2$	1904	34	2.0	74.8	5.8×10^{-2}	$\bar{3}.412$	$\bar{2}.342$
2	Sat. $Mg(OH)_2$	1440	34	1.5	56.1	0.746×10^{-4}	$\bar{6}.516$	$\bar{5}.765$
2	NaCl	50	35	1.5	56.1	1.686×10^{-6}	$\bar{7}.696$	$\bar{7}.765$
1.1	NaOH	268	34	1.5	56.1	3.78×10^{-1}	$\bar{3}.725$	$\bar{2}.644$
1.1	NaOH + Quartz Powder (0.5g)	261	34	1.5	56.1	3.78×10^{-1}	$\bar{3}.712$	$\bar{2}.630$
2	NaCl	73	36	1.5	56.1	1.7×10^{-6}	$\bar{6}.298$	$\bar{7}.693$
2	NaCl	61	36	1.5	56.1	1.7×10^{-6}	$\bar{6}.312$	$\bar{7}.705$

§ 4. Result of Experiment

Table 3 shows the result of the experiment. The third column gives the time of contact of aqueous radioactive solution with chloroform in the sealed quartz tube. The subsequent column "Aqueous HCl*" gives the radioactivity of 1 cc sample before contact directly measured as described in § 1 inclusive of background count, the associated background count, pH before or after the contact at 100°C calculated from that measured directly at room temerature shown in parentheses for solution (i), § 1 or from known solubility of solid hydroxide, contact time, and the decomposition rate for solution (ii), § 1, the total quantity of chloride ion before or after contact, its volume v^S at room temperature and various additions; "Sat. $Ca(OH)_2$" etc. mean the saturation of solution with solid $Ca(OH)_2$ etc. Quantity n_0^S of chloride ion before contact was that calculated from specified concentration and known dilution of the US AEC radioactive hydrogen chloride sample mentioned in § 1 and from the known amount of added chloride, if any. That n^S after contact was the sum of n_0^S and the increment Δn of chloride ion during the contact. The increment in (i) was the rate $[\dot{\mathrm{Cl}}^-]$ of increase of $[\mathrm{Cl}^-]$, given in a subsequent column, multiplied by v^S and the time of contact t, except in the case of run 8, when Δn was the decrease of hydroxide ion titrated directly. The increment in (ii) was that calculated just as described above in § 1.

The next column "Chloroform" shows the directly observed radioactivity of chloroform after contact inclusive of the background count, the associated background count, its volume v^C before contact at room temperature and $-\dot{n}_C/v^S$ at the mean of pH's before and after contact quoted from result in subsequent paper.

The last column "Rates" shows $\log_{10} u_D$ and $\log_{10} u_S$ calculated according to (3.7) from data given in the foregoing columns.

We will now proceed in commenting upon the runs in succession. Run 1 was conducted with the diluted acidic solution of the original sample without any addition: the result is, as shown in the Table, a definite exchange accompanied by a slight shift of pH. Run 2 resulted in exchange as well as in an appreciable pH-shift at higher pH. Run 3 resulted in a practically imperceptible exchange during the same period of contact with nearly neutral solution, in spite of a definitely perceptible pH-shift. Considerable length of contact time of run 4 caused, however, a perceptible exchange accompanied by an appreciable pH-shift from neutral to acidic region.

A pronounced exchange resulted in run 5 by upholding pH at higher value from 10.5 to 9.6 by saturating the solution with solid $Ca(OH)_2$. It was not successful in run 6 or 7 similarly to keep up high pH by means of solid $Ba(OH)_2$ or AgOH respectively, perhaps, because the added amount of them fell short of coping with the decomposition, although qualitatively it was indicated that the exchange was appreciably accelerated at higher pH.

On the basis of the above qualitative survey, the exchange rate was now quantitatively investigated in runs from 8 to 19 with special reference to the effect of pH, the chloride ion concentration and the wall area, confining the associated pH-shift possibly to a narrow range, either by shortening the contact time or by adding solid hydroxides; chloride ion was increased by addition of sodium chloride in runs 11, 15, 18 and 19 or the wall area multiplied in run 17 by addition of quartz powder.

Some of above results are associated with a certain inaccuracy owing to the classical calculation of pH ignoring the deviation of activity coefficients from unity. The activity coefficient of hydrogen ion remains however of the order of magnitude of unity according to the observation of KISS and URMANCY[7] even at the highest concentration of neutral salt (4.0 N NaCl) in the present experiment. Attributing now the deviation to the same extent from unity to other activity coefficients, it might be taken that the error in pH thus introduced is not so much as to be of the magnitude of unity.

The calculation of the present results in the alkaline region is also associated with the inaccuracy of contact time measurement and of $\Delta[Cl^-]$-determination, $\Delta[Cl^-]$ entering the exchange rate expression (3.7) as the correction for the accompanying decomposition.

The contact time of approximately 1 minute in the extreme case of strong alkaline solution is not at all accurate, nevertheless the error introduced in u_D or u_S from this cause could never be that of the order of magnitude.

The $\Delta[Cl^-]$-determination in run 8 of Table 3 is accurate according to the result of subsequent paper[5], that the titrated decrease of hydroxide ion is equivalent to $\Delta[Cl^-]$, as it should be, if chloroform does not practically yield formate by decomposition.

The $\Delta[Cl^-]$ was determined classically in conjunction with the associated pH-change in the case of solution (ii) after contact.*) Correctness of the calculation might be examined below with reference to the decomposition experiment in the subsequent paper, run 3 and 4 of Table 3 there, in which chloroform was kept in contact with solution saturated with $Ca(OH)_2$ or $Mg(OH)_2$ at 100°C and the associated $\Delta[Cl^-]$ followed by titration. Table below shows $\Delta[Cl^-]$ calculated classically just similarly as above ($\Delta[Cl^-]_{calc.}$) side by side with $\Delta[Cl^-]$ directly observed by titration ($\Delta[Cl^-]_{obs.}$).

It might be expected from the contrast between $\Delta[Cl^-]_{calc.}$ and $\Delta[Cl^-]_{obs.}$ in the Table, that $\Delta[Cl^-]_{calc.}$ thus worked out is correct at least in order of magnitude. It is seen from

---

*) Cf. foot-note **) on page 121.

Runs in Table 3 in Subsequent Paper[5)]	Additions	$\Delta[Cl^-]_{calc.}$ mol/ℓ	$\Delta[Cl^-]_{obs.}$ mol/ℓ
3	Sat. $Ca(OH)_2$	0.12	0.068
4	Sat. $Mg(OH)_2$	0.0045	0.0055

(3.7) on the other hand that u_S does not practically shift with $-\dot{n}^Ct$ or with $\Delta[Cl^-]$, whereas u_D increases less than proportional to the latter, inasmuch as $-\dot{n}^Ct$ is practically negligible compared with $n_0{}^C$ but considerably larger than $\dot{n}_0{}^S$ in runs 5, 8, 12, 13, 14, 16 and 17, where the effect of $\Delta[Cl^-]$ is in question. It is hence expected that u_S or u_D in this case is correct at least in order of magnitude and may be incorporated with other more exact measurements, with due regard to the associated inaccuracy, in determining the dependence of u_D or u_S on pH or $\Delta[Cl^-]$.

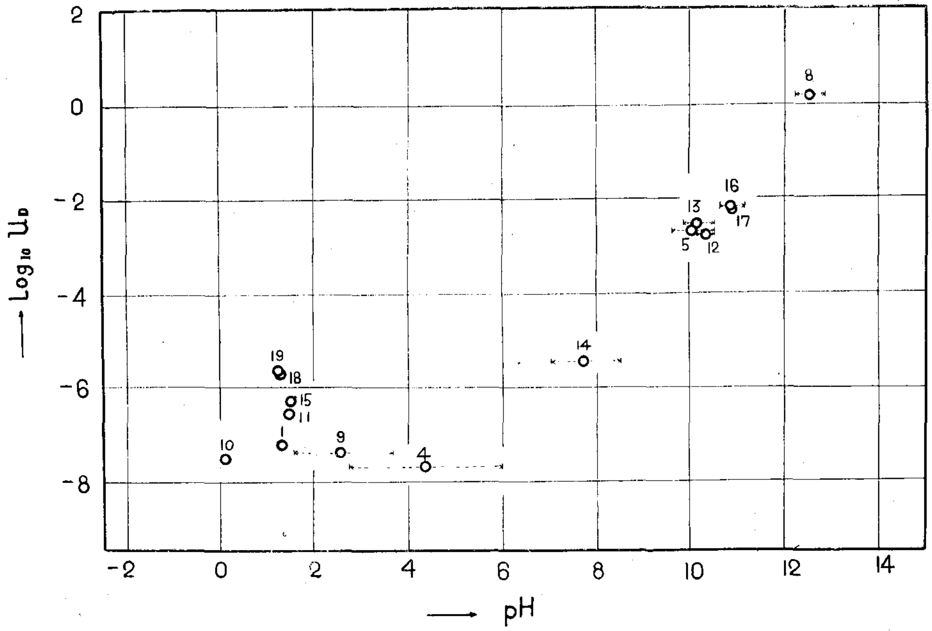


Fig. 1 Rate $u_D \equiv r$ mol Cl/lit. min. of Chlorine Transfer From Solution to Chloroform in One Direction, 100°C.

|←--------→| :—Range of pH-Variation.

The $\log_{10} u_D$ and $\log_{10} u_S$ are now plotted respectively in Figs. 1 and 2 against pH at the middle of its range of variation, if any, during the contact, shown each by a horizontal dotted line. It is seen from Fig. 1 that u_D varies not only with pH but with $[Cl^-]$ by a factor more than 10^2, whereas from Fig. 2 that u_S varies virtually as a sole function

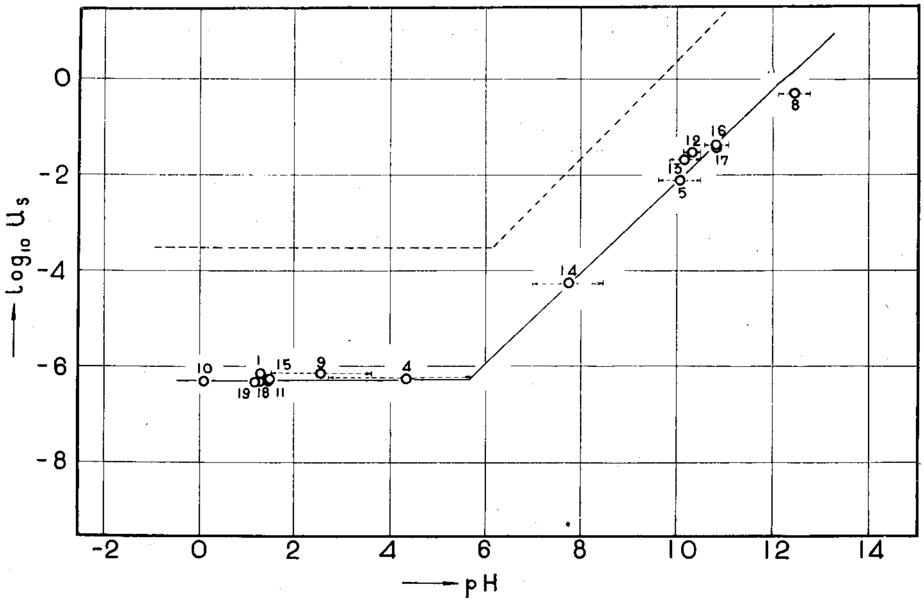


Fig. 2 Specific Rate $r/[Cl^-]$ min.$^{-1}$ of Chlorine Transfer From Solution to Chloroform in One Direction, 100°C.
$|\leftarrow \text{- - - - - - - -} \rightarrow|$:—Range of pH-Variation.

of pH independent of $[Cl^-]$ as well as of wall area. A straight line with a break is drawn through observed points as in Fig. 2 in compliance with the different precisions of data considered above. Dotted line "H-Exchange" in Eig. 2 shows, for comparison, the recent result of Kaneko and Sato6) on hydrogen exchange between chloroform and solution at the same condition.

It is now concluded from the above results that the exchange rate r is proportional to $[Cl^-]$, the appropriate proportionality factor u_S being sole function of pH independent of $[Cl^-]$, of wall area and even of pH up to pH 6.0, whence it increases inversely proportional to the activity of hydrogen ion.

On the basis of these results it might be admitted that the reaction proceeds homogeneously in the interior of the solution and that the dissolution of chloroform into the solution and its reversal are not controlling. Incidentally we see from the result that the neglect of temperature variation in § 1 of low value of pH, hardly affects the conclusion, even if it caused more or less error in estimation of pH at 100°C at all, because of $\log_{10} u_S$ being virtually constant at lower pH.

§ 5. Chlorine Exchange and Decomposition

The mechanism of chlorine exchange will be discussed on the basis of the results in the foregoing section assuming the existence of its controlling step (abbreviated to CSCE in what follows). It is implied in the statement that CSCE does exist that no exchange*) whatever takes place without its occurrence and that if it once occurred, the exchange*) proceeds practically to completion.

For the latter "sufficient" condition to be fulfilled, however, other steps than the CSCE responsible for the exchange should be occurring back and forth much more frequently than the CSCE is, so that the steps are practically in exchange equilibrium**).

If for instance the exchange between chloride ion in solution and chloroform proceeds through steps,

$$\mathrm{CHCl_3} \xrightarrow{\qquad} \mathrm{CHCl}_{3\,aq.} \qquad \text{(a)}$$

$$\mathrm{CHCl}_{3\,aq.} \xrightarrow{\qquad} \mathrm{CCl_3^-} + \mathrm{H^+} \qquad \text{(b)}$$

$$\mathbf{Cl}^- + \mathrm{CCl_3^-} \dashrightarrow \mathbf{Cl}\mathrm{CCl_2^-} + \mathrm{Cl^-} \qquad \text{(c)}$$

and if (b) is the CSCE, then steps (a) and (c) must practically be in exchange equilibrium, where **Cl** denotes chlorine atom of chloride ion in solution in distinction from that in chloroform, $\mathrm{CHCl}_{3\,aq.}$ chloroform dissolved in solution and $\mathrm{CHCl_3}$ that in its practically pure phase in the reaction vessel.

We will first consider the case when chlorine exchange takes place through the rate-determing step of decomposition in either direction. The CSCE must then be either the rate-determining step itself or its reversal according to the definition of CSCE*), since no other step in exchange equilibrium by definition could ever be the rate-determining step of the decomposition. In the case when CSCE is the rate-determining step of decomposition, r must equal the forward rate***) of the rate-determining step and therefore be either practically equal to or greater than the overall decomposition rate***) $-[\dot{\mathrm{Cl}}^-]$, i.e., the excess

---

*) Transfer of chlorine atom from solution to chloroform. Cf. foot-note on page 123.

**) The "exchange equilibrium" is defined as that in which forward and backward rates of transfer are balanced with each other with respect to individual isotopes involved in distinction from the simple equilibrium, in which the rates are balanced as a whole but not necessarily individually.

***) Every rate in this paper is expressed in terms of associated transfer of chlorine atom but not of chloroform molecule as in the subsequent paper. The former rate is three times the latter.

of the forward rate over the backward one of the rate-determining step.

The $[\dot{\mathrm{Cl}}^-]$ or u_S has been found respectively constant in the subsequent[5] or in the present paper at lower pH throughout the whole observed $[\mathrm{Cl}^-]$-range. Table 4 summarizes observed $[\dot{\mathrm{Cl}}^-]$ with or without addition of neutral salt, the appropriate range of pH-variation, that of $[\mathrm{Cl}^-]$, and $u_S[\mathrm{Cl}^-]$, the product of average $u_S = 5.8 \times 10^{-7}$ mol/lit. min. over the pH-region where u_S is practically constant independent of pH and the mean of initial and final $[\mathrm{Cl}^-]$ given in the fourth column of the Table.

Table 4 shows that $u_S[\mathrm{Cl}^-]$ or r at lower $[\mathrm{Cl}^-]$ than 0.356 N is appreciably less than $[\dot{\mathrm{Cl}}^-]$, which excludes the possibility of CSCE being the rate-determining step itself.

Neither is the alternative case of CSCE being the reversal of the rate-determining step valid, as shown below.

TABLE 4 Decomposition and Exchange Rate

5.8×10^{-7} min.$^{-1}$*)

No.	pH	$[\dot{\mathrm{Cl}}^-]$ mol Cl/lit. min × 10^6	$[\mathrm{Cl}^-]$ mol/lit.	u_S $[\mathrm{Cl}^-]$ mol Cl/lit. min × 10^6	Addition	Reference to Subsequent Paper
1**)	0.1 ~3.2	1.65	0 ~0.0032	0.009	None	Tab. 1, 3
2	2.90~4.15	1.8	0.354~0.356	0.21	0.35 N NaCl	Ser. 1, Tab. 2
3	3.25~4.12	2.2	0.010~0.011	0.060	0.01 N NaCl	Ser. 4, Tab. 2
4	3.25	1.6	0 ~0.00052	0.003	0.01 N $\mathrm{Na_2SO_4}$	Ser. 5, Tab. 2
5	1.89~1.78	1.7	4.00 ~4.01	2.3	4.0 N NaCl	Run 11, Tab. 3
6	2.00~1.96	1.8	0.0038	0.011	5.2 N $\mathrm{Na_2SO_4}$	Run 12, Tab. 3

*) Average of u_S-values of runs 1, 4, 9, 10, 11, 15, 18 and 19 in Table 3.

**) This number indicates the average data of decomposition measurements of the subsequent paper [Ref.5] without addition of neutral salt at pH below 3.2, where $[\dot{\mathrm{Cl}}^-]$ is found practically constant independent of pH. The $[\dot{\mathrm{Cl}}^-]$ of this number is the average of $[\dot{\mathrm{Cl}}^-]$-values each of series 3, 5, 7 and 8 of Table 1 and of runs 5, 6, 7, 8 and 10 of Table 3 of the subsequent paper each with equal weight; $[\dot{\mathrm{Cl}}^-]$ was determined for each series in the former group of measurements by analysis of pH-variation with time and in latter by titration of liberated chlorine; $[\dot{\mathrm{Cl}}^-]$-value here of each series is the mean over those determined for each pH below 3.2 given in Table 5 there in the subsequent paper.

Let j be the rate-determining step of the decomposition. The steady rate $[\dot{\mathrm{Cl}}^-]$ of decomposition is the forward rate $\vec{v}_j$ of j minus the backwared one now equated to the exchange rate according to the premise. Expressing the exchange rate by $u_S[\mathrm{Cl}^-]$ according to the conclusion in §4, we have,

$$[\dot{\mathrm{Cl}}^-] = \vec{v}_j - u_S[\mathrm{Cl}^-] \tag{5.1}$$

The $u_S[\mathrm{Cl}^-]$ of experiments No. 1, 3, 4 and 6 in Table 4 is negligibly small compared with $[\dot{\mathrm{Cl}}^-]$, while the latter is constant irrespective of different additions of neutral salts. It follows according to (5.1) that $\vec{v}_j$ must also be constant at least under the conditions of these experiments.

The forward rate $\vec{v}$ of a step in homogeneous fluid is expressed in general as,

$$\vec{v} = k\mathfrak{A}^{\delta^I} {}^{*)} \tag{5.2}$$

where $\mathfrak{A}^{\delta^I}$ is the absolute activity or the reciprocal BOLTZMANN factor of the chemical potential of the initial complex**); k is the "rate constant" common to the forward and backward rates and actually constant at infinite dilution of components of variable concentrations.

The $k_j\mathfrak{A}^{\delta^I_j}$ written particularly for $\vec{v}$ of the rate-determining step j is now constant irrespective of different addition of neutral salts at least in above numbers of experiments. As shown in the subsequent paper***) the particular value $\mathfrak{A}_S^{\delta^I_j}$ assumed by $\mathfrak{A}^{\delta^I_j}$ at the steady state equals practically its upper limit $\mathfrak{A}_{e,j}^{\delta^I_j}$, as j determines the rate and every one of series S of steps of decomposition which brings a set $\delta^{I'}_j$ of stable molecules and ions****) down to δ^I_j is in equilibrium,***) so that, if n_C pieces of chloride ion are liberated algebraically by the resultant of S in bringing about δ^I_j from $\delta^{I'}_j$, $\mathfrak{A}_{e,j}^{\delta^I_j}$ and hence $\mathfrak{A}_S^{\delta^I_j}$ varies proportionally to $(\mathfrak{A}^{\mathrm{Cl}^-})^{-n_c}$.

It is seen from Table 4 that $u_S[\mathrm{Cl}^-]$ is more than six folded or reduced to one third from No. 1 to 3 or to 4 respectively, while $[\dot{\mathrm{Cl}}^-]$ or $k_j\mathfrak{A}_{e,j}^{\delta^I_j}$ remains tolerably constant with regard to the error involved in $[\dot{\mathrm{Cl}}^-]$-determination of No. 3.*****) This effect cannot be due to some compensation of the variation of $\mathfrak{A}_{e,j}^{\delta^I_j}$ proportional to $(\mathfrak{A}^{\mathrm{Cl}^-})^{-n_c}$ by that of k_j due to the neutral salt, admitting that the latter's effect, if any, is first of all that of ionic interaction and that the addition of 0.01 N NaCl or of 0.01 N Na_2SO_4 shifts k_j, if at all, in the same direction. It follows that k_j and $\mathfrak{A}_{e,j}^{\delta^I_j}$ must individually be constant irrespective of neutral salt addition. This conclusion is supported by No. 6 of $[\mathrm{Cl}^-]$ remaining unaffected by an extremely high concentration 5.2 N of Na_2SO_4.

The forward rate $\vec{v}_j$ must hence be around 1.7×10^{-6} even in the case of No. 5 of

---

*) Cf. §5 of the subsequent paper [Ref. 5).]

**) Set of particles involved in the step at the state before its occurrence.

***) Cf. §6, Ref. 5).

****) Those ones other than intermediates of decomposition.

*****) The $[\dot{\mathrm{Cl}}^-]$ is determined in this case by differentiating $[\mathrm{Cl}^-]$ determined from observed pH with respect to time. The value of $[\dot{\mathrm{Cl}}^-]$ thus obtained is less accurate than that of titration as judged from its fluctuation.

4 N NaCl addition in Table 4. This conclusion contradicts, with regard to (5.1), the fact that [Cl^-] then remains constant at 1.7×10^{-6}, while u_g[Cl^-] amounts to even more than the latter, invalidating the underlying premise that CSCE is the reversal of the rate-determining step.

It is however possible besides, that some step subsequent to the rate-determining one in the series of steps responsible for the decomposition may be irreversible just as a dam keeping up a pool beyond may make a rapid stream behind and that one of such steps make the CSCE. If at all, however, the exchange must go through the rate-determining step as well for the chlorine atom picked up from the solution by the reversal of the irreversible step to get into chloroform in discordance with the present premise of unique CSCE, unless the intermediate involved in the irreversible step transmits the chlorine atom somehow to chloroform the other way round. Latter case will be excluded without further discussion in accordance with the conclusion in the subsequent paper*) that such an intermediate has an extremely low activity at the establishment of the rate-determining step.

§ 6. CSCE in equilibrium

It follows from the conclusion arrived at in the foregoing section that CSCE is practically in equilibrium or that its rates in both the directions are balanced with each other, inasmuch as the decomposition of chloroform is only the process proceeding irreversibly in our assembly.

We may now call either of the complexes converted from each other by the balanced steps of CSCE the initial complex and the other the final one at our disposal, inasmuch as either behaves in kinetically identical manner because of the equilibrium relation, although it might be legitimate in accordance with our definition of exchange rate**) to attribute the final complex to the one which converts into a set δ' of stable molecules and ions including chloroform through a series of steps in exchange equilibrium***); in the particular case when both the complexes are of identical configuration as in (3.5. *S*), any particularity of either vanishes of course. Such step will be called a symmetric one. At any rate either or both of the two complexes must convert into δ' through steps in exchange equilibrium, since otherwise the exchange reaction in accordance with our premise in § 5 would not proceed at all.

---

*) Cf. § 6. Ref. 5).

**) Cf. § 3.

***) Steps involved in exchange reaction other than the CSCE are assumed in exchange equilibrium Cf. § 5.

We will call the complex, which converts into δ' through steps in exchange equilibrium, the initial complex δ^I of CSCE and denote the appropriate δ' by $\delta^{I'}$.

We have now, according to the definition of absolute activity in the foregoing section,

$$\mathfrak{A}^{\delta^I} = \mathfrak{A}^{\delta^{I'}}$$

or according to (5.2),

$$r \propto \mathfrak{A}^{\delta^{I'}} \tag{6.1}$$

We shall investigate the constituents of $\delta^{I'}$ and hence of δ^I in the subsequent section on the basis of the kinetic relation (6.1).

§ 7. Dependence of r on pH

It follows immediately from the observed proportionality of r to $[Cl^-]$ identified with the relevant activity, that $\delta^{I'}$ includes only one chloride ion. The $\delta^{I'}$ may be taken, on the other hand, not to include carbon monoxide or formic acid, since there is no sign of drift of exchange rate as seen from Table 3 along with the accumulation, indicated by pH-shift, of these decomposition products.

The $\delta^{I'}$ may include one or more chloroform molecules. It will be assumed to be only one included in $\delta^{I'}$, no experimental material being available at present for deciding this point.

The transition from $\delta^{I'}$ to δ^I should not imply any step either of discharging original chlorine atom of the chloroform molecule involved, in the form of chloride ion into solution or of uptaking to afford it an equal position to that of the original chlorine atoms, since otherwise the specified CSCE would no more be "necessary" in contradiction to its premise. The original proton of chloroform may, however, be given off or that in solution uptaken in this regard.

The δ^I must then include, besides possibly other molecules and ions, $Cl^- + CHCl_3$ or $Cl^- + CCl_3^-$ or $Cl^- + CHCl_3(H^+)_m$, which is represented by SH in what follows, where $CHCl_3(H^+)_m$ is chloroform molecule to which m protons are attached If δ^I consists of SH alone, the corresponding $\delta^{I'}$ is (a) $Cl^- + CHCl_3$ or (b) $Cl^- + CHCl_3 - H^+$ *) or (c) $Cl^- + CHCl_3 + mH^+$ respectively. The rate of the CSCE and hence r must then be, according to (6.1), (a) independent of a^{H^+} or (b) inversely proportional to a^{H^+} or (c) proportional to m-th power of a^{H^+} so that in

---

*) The minus sign of H^+ means that the proton is discharged from a constituent of $\delta^{I'}$, i. e., $CHCl_3$ in its course of forming δ^I.

none of these cases is the pH-dependence of Fig. 2 accounted for.

Including now acid or base or both in δ^I and assuming that acids are H_2O and H_3O^+, and bases OH^- and H_2O respectively exclusively in the aqueous solution just as in the previous work,[1] the pH-dependence of r is given as being one of three types,

$$\frac{r}{a^{SH}} = k_A^W + k_A^{H^+} a^{H^+} \tag{7.1.I}$$

$$\frac{r}{a^{SH}} = k_B^W + k_B^{OH^-}/a^{H^+} \tag{7.1.II}$$

$$\frac{r}{a^{SH}} = k_{AB} + k^{H^+} a^{H^+} + k^{OH^-}/a^{H^+} \tag{7.1.III}$$

where a^{SH} or a^{H^+} is the activity of SH or H_3O^+ respectively of usual scale identified with the respective concentration at infinite dilution and k_A^W etc. are respectively constants*) independent of a^{H^+}.

We see immediately that none of above three types fits in with the observed pH-dependence, if a^{SH} were proportional to $(a^{H^+})^m$ or SH consisted in $Cl^- + CHCl_3(H^+)_m$, so that this case, extraordinarily improbable even otherwise, falls formally out. Similar consideration excludes further the case of $SH \equiv CHCl_3 + Cl^-$ in (7.1.I), when a^{SH} is independent of a^{H^+} and that of $SH \equiv CCl_3^- + Cl^-$ in (7.1.II), when a^{SH} is inversely proportional to a^{H^+} according to (6.1), so that we are left with four possible δ^I's shown in Table 5, where K_C is the dissociation constant of chloroform, i.e.,

$$K_C = a^{CCl_3^-} a^{H^+} / a^{CHCl_3} \tag{7.2}$$

TABLE 5 Possible δ^I and Appropriate pH-Dependence of Rate

Notation of Type of Steps	δ^I		pH-dependence of r/a^{CHCl_3}
	SH	Constituent Acid or Base	
I	$CCl_3^- + Cl^-$	AH	$(k_A^W/a^{H^+} + k_A^{H^+}) K_C$
II	$CHCl_3 + Cl^-$	B	$k_B^W + k_B^{OH^-}/a^{H^+}$
IIIa	$CHCl_3 + Cl^-$	AH + B	$k_{AB} + k^{H^+} a^{H^+} + k^{OH^-}/a^{H^+}$
IIIb	$CCl_3^- + Cl^-$	AH + B	$(k_{AB}/a^{H^+} + k^{H^+} + k^{OH^-}/(a^{H^+})^2) K_C$

---

*) The k_A^W or $k_A^{H^+}$ is the rate constant of the proton acceptance of SH from acid H_2O or H_3O^+ respectively and k_B^W or $k_B^{OH^-}/K_h$ that of proton donation to base H_2O or OH^- respectively; k_{AB} is the sum of rate constants of prototropy for the acid-base pair of H_2O and H_2O or of OH^- and H_3O^+ respectively, and k^{H^+} or k^{OH^-}/K_h for that of H_3O^+ and H_2O or of H_2O and OH^- respectively.

$\mathrm{III_a}$ or $\mathrm{III_b}$ may be one of the possible cases only when the term $k^{\mathrm{H}^+}a^{\mathrm{H}^+}$ or $k^{\mathrm{OH}^-}/(a^{\mathrm{H}^+})^2$ is respectively negligibly small throughout the pH-range of present observation. In the next section will be investigated the ratio of constants k^{H^+} and k^{OH^-} for determining valid δ^I.

§ 8. Ratio of Constants k^{H^+} and k^{OH^-}

The constant k^{H^+} is the rate of the step,[*)]

$$\mathrm{H_2O+SH+H_3O^+} \longrightarrow \mathrm{H_3O^+ + S'H + H_2O} \qquad (8.1.\mathrm{H}^+)$$

at unit activity of hydrogen ion and of substrate SH, i. e., that of the simultaneous attack of base H_2O and acid H_3O^+ to give rise to the "prototropy" of Lowry[8)] transforming SH in general to its isomeric or dissociated state S'H.

The k^{OH^-}/K_h is similarly the rate of the step,

$$\mathrm{OH^- + SH + H_2O} \longrightarrow \mathrm{H_2O + S'H + OH^-} \qquad (8.1.\mathrm{OH}^-)$$

at unit activity of hydroxide ion and of substrate SH, where K_h is the dissociation constant of water.

We see that the acid and base involved in the initial complex of $(8.1.\mathrm{H}^+)$ or of $(8.1.\mathrm{OH}^-)$ are conjugated with each other in either case, so that they are commonly expressed by the scheme.

$$\mathrm{B+SH+H^+B} \longrightarrow \mathrm{BH^+ + S'H + B}$$

The k^{H^+} or k^{OH^-}/K_h may on the other hand be expressed as,

$$k^{\mathrm{H}^+} = C\exp\left(-\frac{\Delta F^*(\mathrm{H_2O})}{RT}\right) \qquad (8.2.\mathrm{H_2O})$$

$$k^{\mathrm{OH}^-}/K_h = C\exp\left(-\frac{\Delta F^*(\mathrm{OH}^-)}{RT}\right) \qquad (8.2.\mathrm{OH}^-)$$

where C is the common factor,[**)] $\Delta F^*(\mathrm{H_2O})$ or $\Delta F^*(\mathrm{OH}^-)$ respectively the appropriate activation free energy or the free energy increment of the whole assembly associated with the formation of a critical complex δ^* from the respective initial complex δ^I reckoned to 1 mol or the reversible work required for the process.

---

*) Cf. foot-note on page 137.

**) Cf. foot-note *) on page 139,

The difference $\Delta F \equiv \Delta F^*(H_2O) - \Delta F^*(OH^-)$ may be taken particular to the set of B's, i. e., that of H_2O and OH^- respectively in (8.2. H_2O) and (8.2. OH^-) but independent of the sort of substrate SH, if one takes only the contribution to ΔF of the direct action of B and S upon H^+ or H, perhaps intervening between B and S, only into account but neglects the difference of the contribution of interaction between, perhaps remoter, B and S due to the difference of S of SH. It then follows from (8.2) that,

$$k^{H^+}/k^{OH^-} = \frac{1}{K_h} \exp\left(-\frac{\Delta F}{RT}\right) \qquad (8.3)$$

or the ratio of catalytic coefficients, k^{H^+} and k^{OH^-}/K_h**) respectively of hydrogen and hydroxide ion, should remain approximately constant at a definite temperature independent of the sort of substrate.

Table 6 shows ΔF derived from reliable data of catalytic coefficients according to (8.3) attributing to all of these cases the prototropic mechanism (8.1); ΔF is approximately constant as shown in the Table and lies within the limits 5 ± 3 Kcal throughout different substrates as expected and even throughout different temperatures except in the case of the depolymerization of dimeric dihydroxyacetone and the racemization of *l* trans-$\alpha\gamma$-dimethyl glutaconic acid.

It might be questioned whether the simple prototropic mechanism is adequate especially to the latter two reactions of complicated molecules. In this connection we might quote the conclusion arrived at in the subsequent paper[5)] that the step,

$$B + HCl{}^{\times}_{\times}CCl_2{}^{***)} + HA \longrightarrow BH^+ + CCl_2 + ClH + A^-$$

---

*) Rate $\vec{v}$ of a step, heterogeneous or homogeneous, is expressed in general [Cf. HORIUTI; Jour. Res. Inst. Catalysis, Hokkaido Univ. **1**, 8 (1948), § 24] as,

$$\vec{v} = \kappa \frac{kT}{h} p^{\delta^*}/p^{\delta^I}$$

where p^{δ^*} or p^{δ^I} is the BOLTZMANN factor of the chemical potential [ibid., § 2] of the critical complex δ^* [Cf. § 23 ibid.] or δ^I respectively, i. e., the reciprocal absolute activity. The ratio $p^{\delta^*}/p^{\delta^I}$ being $\exp\left(-\frac{\Delta F^*}{RT}\right)$ by definition, the factor $\kappa \frac{kT}{h}$ corresponds to C, which is common to all steps provided that the transmission coefficient κ is universal, as assumed here.

**) This gives the catalytic coefficient of hydroxide ion usually denoted simply by k^{OH^-} or the coefficient of the activity of hydroxide ion in the expression of r/a^{SH}, as seen from (7.1. III) remembering $K_h = a^{H^+}a^{OH^-}$.

***) Hydrogen chloride combined with carbon dichloride by coordinate bond or an isomer of chloroform. Cf. § 12. of Ref. 5).

duly of the prototropic type has $\log_{10} k^{H^+}/k^{OH^-}$ -value, i.e.,

$$\log_{10} k^{H^+}/k^{OH^-} = 10.4^{*)}$$

at 100°C, which lies just between the limits,

$$\log_{10} k^{H^+}/k^{OH^-} = 11.1 \sim 7.6 \qquad (8.4)$$

corresponding to those 5±3 Kcal of ΔF at the temperature.

§ 9. δ^I of CSCE

With regard to III_a of Table 5 attributed to the observed pH-dependence of Fig. 2, either k_{AB} or k^{OH^-}/a^{H^+} must be predominant according as pH is below or above 6, at which the straight line through observed points in Fig. 2 breaks, while $k^{H^+}a^{H^+}$ must remain negligible throughout the observed pH-range from 0.1 to 12.7. The terms k_{AB} and k^{OH^-}/a^{H^+} hence equal each other at the break, so that,

$$k_{AB} = 10^6 k^{OH^-}$$

But since,

$$k^{H^+}/k^{OH^-} = 10^{11.1} \sim 10^{7.6} \qquad (9.1)$$

at 100°C as deduced in the foregoing section, we have,

$$k_{AB}/k^{H^+} = 10^{-5.1} \sim 10^{-1.6}$$

which shows that $k^{H^+}a^{H^+}$ is by no means negligible compared with k_{AB} at pH below 1.6 in contradiction to the above requirement.

It is similarly required with regard to III_b of Table 5, that $k^{OH^-}/(a^{H^+})^2$ is negligible compared with k^{H^+}, i.e.,

$$k^{OH^-}/(a^{H^+})^2 \ll k^{H^+}$$

or by (9.1),

$$(a^{H^+})^2 \gg 10^{-7.6}$$

which is not fulfilled altogether at pH below 3.8.

Both III_a and III_b of Table 5 being thus ruled out, there remain two possible δ^I's of CSCE, *viz.*,

$$\delta^I = Cl^- + CCl_3^- + HA \qquad (9.2.\ I)$$

and

$$\delta^I = Cl^- + CHCl_3 + B \qquad (9.2.\ II)$$

---

*) This value corresponds to the idealized pH-dependence derived from the directly observed one with correction for the neutral salt effect.

TABLE 6 Ratio k^{H^+}/k^{OH^-} for Various Reactions

Reactions	Temperature °C	$\log_{10} k^{H^+}/k^{OH^-}$	ΔF Kcal	References
Iodination of acetone	25	9.7	6	9
Iodination of mesityl oxide	25	11.4	4	10
Hydrolysis of methyl dl-glycerate	70.2	8.3	7	11
" ethyl "	"	8.6	7	"
" n-propyl "	"	8.7	6	"
" iso-propyl "	"	9.0	"	"
" n-butyl "	"	8.7	"	"
" iso-butyl "	"	"	"	"
" n-amyl "	"	"	"	"
" iso-amyl "	"	"	"	"
Hydrolysis of dihydroxypropyl acetate	55	9.8	5	12
" propionate	"	9.9	"	"
" n-butyrate	"	"	"	"
" iso-butyrate	"	10.0	"	"
" n-valerate	"	9.9	"	"
" iso-valerate	"	10.0	"	"
Depolymerization of dimeric dihydroxyacetone	25	6.4	10	13
Depolymerization of dimeric glycollaldehyde	25	8.0	8	14
Hydrolysis of ethyl acetate	25	11.0	4	15
Mutarotation of glucose	25	9.6	6	16
Racemization of *l*-trans-αγ-dimethyl glutaconic acid	100	1.5	18	17
Hydrolysis of isopropyl acetate	25	11.3	4	18
" ethyl levulinate	"	10.3	5	19
" benzamide	80	11.6	2	20
" acetanilide	40	12.4	2	"

§ 10. Possible CSCE

It has been concluded in §7 that δ^I of CSCE must preserve the original CCl_3-skeleton of chloroform unimpaired, in so far as CSCE is indispensable for chlorine exchange as defined, but the latter condition does not necessarily require the same of δ^F, inasmuch as the CSCE remains duly indispensable if the skeleton were disrupted in δ^F, provided that the disrution product be restored to chloroform solely through the reversal of CSCE*), thus giving rise to the chlorine exchange. In such a case, the resultant of forward and backward step of CSCE is, in accordance with two possible δ^I's of (9.2),

$$\mathbf{Cl}^- + \mathrm{CCl}_3^- + \mathrm{HA} \xrightarrow{\mathrm{I}} \mathrm{Cl}^- + \mathrm{C}\mathbf{Cl}\mathrm{Cl}_2^- + \mathrm{HA} \qquad (10.1.\mathrm{I})$$

or

$$\mathbf{Cl}^- + \mathrm{CHCl}_3 + \mathrm{B} \xrightarrow{\mathrm{II}} \mathrm{Cl}^- + \mathrm{CH}\mathbf{Cl}\mathrm{Cl}_2 + \mathrm{B} \qquad (10.1.\mathrm{II})$$

where **Cl** denotes the chlorine atom originating from chloride ion possively replacing that Cl from chloroform through the step.

Let the alternative case now be considered when CCl_3-skeleton is not disrupted in δ^F. This state of δ^F is brought down from δ^I through steps in exchange equilibrium just as that of δ^I is and subject to the same condition as that kinetically imposed upon δ^I, inasmuch as the CSCE is in equilibrium or forward and backward rates of CSCE are balanced with each other, so that they must vary just identically with each other with varying factors, pH, $[\mathrm{Cl}^-]$ etc. The conclusion is that all the possible cases of δ^F of CSCE are those of δ^I as given by (9.2) and hence all the possible CSCE in this case are the transitions, I, I′, II and II′ expressed as,

$$\left.\begin{tikzcd}
\mathbf{Cl}^- + \mathrm{CCl}_3^- + \mathrm{H}^+\mathrm{B} \arrow[r, "\mathrm{I}"] \arrow[dr, "\mathrm{I}'"'] & \mathbf{Cl}\mathrm{CCl}_2^- + \mathrm{Cl}^- + \mathrm{H}^+\mathrm{B} \\
\mathbf{Cl}^- + \mathrm{CHCl}_3 + \mathrm{B} \arrow[ur, "\mathrm{II}'"] \arrow[r, "\mathrm{II}"] & \mathbf{Cl}\mathrm{CHCl}_2 + \mathrm{Cl}^- + \mathrm{B}
\end{tikzcd}\right\} \qquad (10.2)$$

where HA of (9.2) is rewritten into its identity $\mathrm{H}^+\mathrm{B}$.

Transitions (10.1. I) and (10.1. II) are included respectively in I and II of (10.2) with an implication that each of the latter symmetric steps may occur as the resultant of the relevant forward and backward acts as well.

All possible CSCE's expressed by (10.2) with this implication will be discussed further in the next section.

---

*) If not, but the disruption product were conveyed back to chloroform through other channel, the CSCE is no more indispensable, the channel accompanying necessarily chlorine exchange.

§ 11. Mechansim of Chlorine Exchange

It is required in cases I, I′ and II′ of CSCE that the step which provides CCl_3^- from chloroform must occur back and forth much more quickly than the respective CSCE does. But since such step accompanies neccesarily the hydrogen exchange of chloroform, it is required if these steps are the CSCE, that the hydrogen exchange must be much more rapid than the chlorine exchange is. This condition is fulfilled as shown by the recent result of KANEKO and SATO⁽⁶⁾ as illustrated by "H-Exchange" in Fig. 2.

It is concluded moreover in the subsequent paper⁽⁵⁾ that the step,

$$CHCl_3+B \longrightarrow CCl_3^- + H^+B \qquad (11.1)$$

is responsible for the observed hydrogen exchange on the basis of the experimental results of the latter, of chloroform decomposition and of chlorine exchange as reported in the present paper. It follows now that two kinds of δ^I as well as those of δ^F of (10.2) are respectively in exchange equilibrium with each other or rapidly converting into each other before entering any step of (10.2).

The critical complex of II or II′ must have, however, many common features in electronic configuration with δ^I of I or I′, inasmuch as B in the former must have done its part of accepting proton in giving rise to the pH-dependence of exchange rate as indicated in Fig 2. The critical complex must hence be scarcely different, whichever δ^I the CSCE may start from.

The state of (9.2. I) exists inasmuch as CCl_3^- does, as concluded in the subsequent paper⁽⁵⁾ in conjunction with the equilibrium of step (11.1). Now let (9.2. II) be taken the valid CSCE. We see now no reasen why a set of particles of the state (9.2. I) should get through the state of (9.2. II), to neutralize CCl_3^- once in the form of chloroform, for arriving at the critical complex of the similar electronic configuration; the state of (9.2. I) might be taken intermediate between those of (9.2. II) and the critical complex.

It is hence reasonable to attribute the state of (9.2. I) to δ^I of CSCE and for a similar reason the same state to its δ^F. This conclusion is not altered, if either or both of (10.2) were the resultant of the relevant forward and backward acts as in the case of (10.1).

Summing up, the conclusion is that the chlorine exchange proceeds through steps,

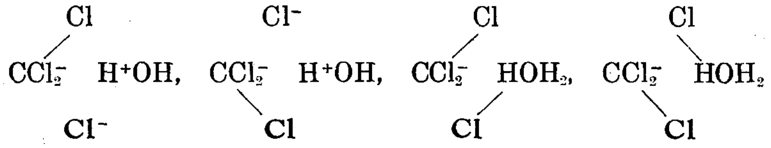
$$CHCl_3 + B \longrightarrow CCl_3^- + H^+B$$

$$Cl^- + CCl_3^- + HA \longrightarrow ClCCl_2^- + Cl^- + HA$$

which are both in equilibrium, the first of which is occurring rapidly back and forth, i.e., in exchange equilibrium giving rise to the much quicker hydrogen exchange.

§ 12. Remarks on the Concluded Mechanism

1. The horizontal part in Fig. 2 is now attributed in accordance with (7.1.1) and (7.2) to $k_A^{H^+}$ and that of -1 inclination to k_A^W/a^{H^+}. It follows that $k_A^{H^+}$ and k_A^W/a^{H^+} approximate each other at the break at pH 6 and hence $k_A^{H^+}$ is 10^6 times as large as k_A^W. This prominence of $k_A^{H^+}$ over k_A^W might be attributed to the reduction of the potential of the critical complex due to the electrostatic interaction between Cl^- and CCl_3^- by the positive charge of H_3O^+ or by the formation of HCl molecule as suggested in a previous paper.[4] Incorporating these, the pronounced "catalytic" activity of H_3O^+ might be referred to the electronic configuration of the critical complex resonating among,



where Cl and **Cl** are symmetrically interchanging their states with each other.

2. It follows from the mechanism as inferred previously[4], that ultraviolet irradiation increases both the hydrogen and chlorine exchange by the same factor, which is yet to be verified.

3. So far it has been assumed that δ^I of CSCE includes only one chloroform molecule; two or more may be involved so far as the present kinetic data are concerned. If two, a similar argument leads to the CSCE,

$$Cl^- + CCl_3^- \cdot CHCl_3 + HA \longrightarrow ClCCl_2^- \cdot CHCl_3 + Cl^- + HA$$

associated with the step,

$$2CHCl_3 + B \longrightarrow CCl_3^- CHCl_3 + H^+B$$

in exchange equilibrium, which supplies $CCl_3^- \cdot CHCl_3$ similarly as (11.1) does CCl_3^-.

The question of the number of chloroform molecules included in $\delta^{I'}$ might rather be left open, until sufficient kinetic data are available.

Summary

1. Chloroform and aqueous chloride solution of different pH with or without addition of NaCl were sealed air-free together in a quartz vessel, shaken briskly at 100°C and the chlorine exchange between them was followed by measuring the radioactivity of the solution and of chloroform respectively before and after the experiment. The pH of the solution was adjusted by addition of sodium hydroxide or of sulfuric acid or of solid hydroxide of magnesium, calcium, barium or silver for retarding, in the latter case, pH-variation caused by decomposition product of chloroform.
2. The exchange rate or the forward rate of transfer of chlorine from solution to chloroform was calculated from the results of the above experiment allowing for simultaneous decomposition; the rate was found proportional to the concentration $[Cl^-]$ of chloride ion present and the appropriate proportionality factor u_S constant at 5.8×10^{-7} min^{-1} independent of pH from 0.1 to 6 and of $[Cl^-]$ from 0.07 to 4.0 N; over pH above 6, u_S increased almost in proportion to the reciprocal activity of hydrogen ion, inclination attaining to the order of magnitude of unity around pH=12 (100°C).

   The chlorine exchange at $[Cl^-]$ below 1 N was much slower than the chloroform decomposition and still more slow than the hydrogen exchange. Its rate was not affected by addition of quartz powder.
3. It was deduced from results of the present and other experiments that exchange takes place through steps in equilibrium and its controlling step (CSCE) involves acid or base or both of them. The ratio of so-called catalytic coefficients of hydrogen ion and hydroxide ion of reaction, which the prototropic mechanism was taken to underlie, was theoretically deduced as lying within narrow limits for different substrates, and the conclusion was demonstrated by numerous examples inclusive of results in the subsequent paper. From these experimental and theorectical results, two possible cases of the initial complex δ^I of CSCE were deduced.
4. A complete set of possible CSCE was developed on the basis of the above conclusion. By the consideration of the electronic configura-

tion of critical complex and of δ^I, the most probable one among them was concluded to be,

$$Cl^- + CCl_3^- + HA \longrightarrow ClCCl_2^- + Cl^- + HA$$

associated with a step, in exchange equilibrium,

$$CHCl_3 + B \longrightarrow CCl_3^- + H^+B$$

which gave rise to rapid hydrogen exchange, where HA or B was the BRÖNSTED acid or base respectively.

References

1) HORIUTI and TANABE, Proc. Japan Acad., **27**, 404 (1951).
2) HORIUTI and TANABE, ibid., **28**, 127 (1952).
3) HORIUTI and TANABE, ibid., **28**, 130 (1952).
4) HORIUTI and TANABE, ibid., **29**, 254 (1953).
5) HORIUTI, TANABE and TANAKA, This Volume p. 147.
6) KANEKO and SATO, to be published.
7) KISS and URNÁNCY, Z. physik. Chem. A **169**, 31 (1934).
8) LOWRY, Trans. Chem. Soc. London, **123**, 828 (1923).
9) DAWSON and SPIVEY, J. Chem. Soc. London, 2180 (1930).
10) DAWSON and KEY, ibid., 2154 (1928).
11) GROOCOCK et al., ibid., 1039 (1930).
12) INGOLD et al., ibid., 2035 (1931).
13) BELL and BAUGHAN, ibid., 1947 (1937).
14) BELL and HIRST, ibid., 1777 (1939).
15) DAWSON and LOWSON, ibid., 2444 (1927).
16) BRÖNSTED and GUGGENHEIM, J. A. C. S. **49**, 2554 (1927).
17) BULL et al., J. Chem. Soc. London, 1653 (1934).
18) SKRABAL et al., Monatsh. für Chem., **47**, 17 (1926).
19) SKRABAL et al., ibid., **45**, 141 (1924).
20) BOLIN, Z. anorg. Chem. **143**, 201 (1925).