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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 6(1), 57-67
Issue Date	1958-07
Doc URL	<a href="http://hdl.handle.net/2115/24671">http://hdl.handle.net/2115/24671</a>
Type	bulletin (article)
File Information	6(1)_P57-67.pdf



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# ON THE MECHANISM OF DECOMPOSITION OF CHLOROFORM IN AQUEOUS SOLUTION AND THE SIMULTANEOUS CHLORINE EXCHANGE BETWEEN THEM.

By

Juro HORIUTI and Meiseki KATAYAMA<sup>\*)</sup>

(Received June 7, 1958)

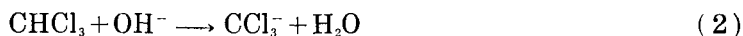
## Introduction

HINE, PEEK and OAKES<sup>1)</sup> have conducted a precise observation on the hydrogen exchange between chloroform and water in aqueous alkaline solution<sup>2)</sup> at 35°C, confirming that the reaction proceeds homogeneously in aqueous phase with the rate proportional to the concentrations of chloroform and hydroxide ion. HINE and DOWELL<sup>3)4)</sup> (HD) have observed the rate of chloroform decomposition in aqueous alkaline solution at the same temperature finding that the rate was similarly proportional to concentrations of chloroform and hydroxide ion but depressed by additions of chloride, bromide and iodide ions.

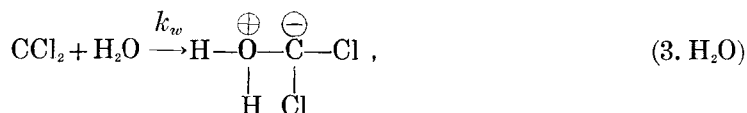
HD concluded from these results<sup>3)4)</sup> that the decomposition is governed by the dissociation



of trichloromethyl anion  $\text{CCl}_3^-$  formed from chloroform by the step<sup>2)</sup>



in preliminary equilibrium and that dichloromethylene  $\text{CCl}_2$  formed by (1) either completes the decomposition through the steps



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or gives rise to the reversal of (1), i. e.



and further, in the presence of iodide or bromide ion, to the similar step,



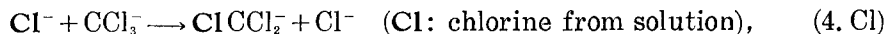
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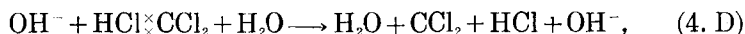
where  $k_1$  etc. denote the rate constants of the respective steps.

The depression of the decomposition rate has been attributed by HD to the acceleration of (3. Cl), (3. I) or (3. Br) by halide ion<sup>4)</sup>, and the chlorine exchange to the penetration of chloride ion from solution into trichloromethyl anion by (3. Cl) and hence into chloroform through the reversal of Step (2)<sup>4)</sup>, assumed rapid enough to be in preliminary equilibrium.

HORIUTI, TANABE and TANAKA (HTT) have observed at 100°C the chlorine exchange between chloroform and aqueous chloride solution saturated with chloroform<sup>5)6)</sup> and the concurrent decomposition in solution over the whole accessible pH-range. The simultaneous hydrogen exchange between chloroform and aqueous solution has been observed by KANEKO and SATO<sup>8)</sup> under the same condition. HTT have deduced the mechanism of the reactions from the results of these experiments over the whole observed pH-range, which states, with particular reference to alkaline solution, that the chlorine exchange is controlled by the step



where trichloromethyl anion  $\text{CCl}_3^-$  is in preliminary equilibrium with chloroform through (2); the latter step is however so quick as being responsible for the rapid hydrogen exchange<sup>5)6)8)</sup> similarly as in HD's mechanism<sup>1)3)4)</sup>, so that  $\text{Cl}^-$  once found its way into trichloromethyl anion penetrates practically with certainty into chloroform. The decomposition in alkaline solution is governed, according to the HTT's mechanism, by the step



where the isomer  $\text{HCl} \times \text{CCl}_2$  of chloroform<sup>(6)(9)</sup> is in preliminary equilibrium<sup>(6)</sup> with chloroform through a few steps inclusive of (2) but not of (4. Cl).

It is the purpose of the present work to appeal to experiments for judging between the two contrasting mechanisms by comparing incompatible conclusions, respectively deduced from them, with experimental results.

### Conclusions Derived from the Contrasting Mechanisms

Conclusions are deduced below from both the mechanisms, assuming that aqueous solution is saturated with chloroform as in the case of HTT's experiments. According to HTT's mechanism the rate of chlorine exchange, i.e. the unidirectional rate  $r$  of chlorine penetrating from solution into chloroform<sup>(6)</sup> is proportional to  $[\text{CCl}_3^-][\text{Cl}^-]$  on account of its rate-determining step (4. Cl) and hence to  $[\text{OH}^-][\text{Cl}^-]$  because of the proportionality of  $[\text{CCl}_3^-]$  to  $[\text{OH}^-]$  maintained by the preliminary equilibrium of (2) and the constant concentration  $[\text{CHCl}_3]$  of saturated chloroform in solution, i.e.

$$u_s \equiv r/[\text{Cl}^-] \propto [\text{OH}^-],$$

where  $[\text{CCl}_3^-]$  etc. are concentrations respectively of  $\text{CCl}_3^-$  etc. The rate of the decomposition, i.e. that of (4. D) is proportional to  $[\text{OH}^-]$ , because of the constant concentration of  $\text{HCl} \times \text{CCl}_2$  sustained by its preliminary equilibrium with saturated chloroform<sup>(7)</sup>. It follows that

$$u_s/V_d = \text{const}, \quad u_s, V_d \propto [\text{OH}^-] \quad (5. a) \quad (5. b)$$

in alkaline solution. These conclusions are however based on the mass action law, from which and hence from (5) more or less deviation is expected as caused especially by the ionic strength effect<sup>(\*)</sup>. The deviation

<sup>(\*)</sup> The rate  $v$  of an elementary reaction is generally expressed [HORIUTI, this Journal 1, 8 (1948); 4, 55 (1956)] as

$$v = ka^I/f^{\ddagger},$$

where  $k$  is virtually constant at constant temperature,  $a^I$  the activity product of the initial complex and  $f^{\ddagger}$  the activity coefficient of the critical complex. The preliminary equilibrium mentioned in the text and the saturation of solution with chloroform assure the strict constancy of  $a^I$  of the rate-determining step of the chlorine exchange and that of the decomposition, rather than the constancy of the corresponding concentration product. Identifying concentrations  $[\text{OH}^-]$  and  $[\text{Cl}^-]$  respectively with the appropriate activities, any deviation from the mass action law is ascribed according to the above equation solely to the variation of  $f^{\ddagger}$  of the rate-determining step.

in alkaline solution is, however, not so much as appreciably to disfigure the above mass law effect in so far as hitherto observed<sup>6)7)</sup>.

According to HD's mechanism, on the other hand, dichloromethylene causes the decomposition of chloroform through (3.H<sub>2</sub>O) and (3.OH) at the rate

$$V_d = (k_w[\text{H}_2\text{O}] + k_h[\text{OH}^-])[\text{CCl}_2], \quad (6. D)$$

while it gives rise through (3.Cl) to the chlorine exchange at the rate

$$r = u_s[\text{Cl}^-] = k_{\text{Cl}}[\text{Cl}^-][\text{CCl}_2], \quad (6. E)$$

or, in the presence of iodide ion, even to the formation of  $\text{CCl}_2\text{I}^-$  ion at the rate

$$r_{\text{I}} = k_{\text{I}}[\text{I}^-][\text{CCl}_2]. \quad (6. I)$$

We have now from (6.D) and (6.E)

$$u_s/V_d = k_{\text{Cl}}/(k_w[\text{H}_2\text{O}] + k_h[\text{OH}^-]) \quad (7)$$

and for the overall rate of consumption of dichloromethylene

$$V_d + r + r_{\text{I}} = (k_w[\text{H}_2\text{O}] + k_h[\text{OH}^-] + k_{\text{Cl}}[\text{Cl}^-] + k_{\text{I}}[\text{I}^-])[\text{CCl}_2],$$

which should equal, at the steady state, the rate  $k_1[\text{CCl}_3^-]$  of its supply by Step (1), i. e.

$$k_1[\text{CCl}_3^-] = (k_w[\text{H}_2\text{O}] + k_h[\text{OH}^-] + k_{\text{Cl}}[\text{Cl}^-] + k_{\text{I}}[\text{I}^-])[\text{CCl}_2]. \quad (8)$$

We have besides by the preliminary equilibrium of Step (2)

$$[\text{CCl}_3^-] = K[\text{CHCl}_3][\text{OH}^-], \quad (9)$$

where  $K$  is the equilibrium constant and hence from (8) and (9)

$$[\text{CCl}_2] = \frac{k_1 K [\text{CHCl}_3][\text{OH}^-]}{k_w[\text{H}_2\text{O}] + k_h[\text{OH}^-] + k_{\text{Cl}}[\text{Cl}^-] + k_{\text{I}}[\text{I}^-]},$$

or by (6)

$$V_d = \frac{k_1 K (k_w[\text{H}_2\text{O}] + k_h[\text{OH}^-]) [\text{CHCl}_3][\text{OH}^-]}{k_w[\text{H}_2\text{O}] + k_h[\text{OH}^-] + k_{\text{Cl}}[\text{Cl}^-] + k_{\text{I}}[\text{I}^-]} \quad (10. V)$$

and

$$u_s = \frac{k_{\text{Cl}} k_1 K [\text{CHCl}_3][\text{OH}^-]}{k_w[\text{H}_2\text{O}] + k_h[\text{OH}^-] + k_{\text{Cl}}[\text{Cl}^-] + k_{\text{I}}[\text{I}^-]}. \quad (10. u)$$

The mechanism of HD thus predicts that  $u_s/V_d$  depends only on  $[\text{OH}^-]$ , while  $V_d$  and  $u_s$  severally decreases with increasing  $[\text{Cl}^-]$  and  $[\text{I}^-]$  by the same factor, because of the decrease of the steady concentration of

dichloromethylene. The  $u_s/V_d$  and the individual variation of  $V_d$  and  $u_s$  with  $[Cl^-]$  or  $[I^-]$  are determined by (7) and (10) from the data

$$k_{Cl}/k_w = 65.7^{(*)}, \quad k_I/k_w = 506^{(*)}, \quad k_h/k_w = 229 \quad (11)$$

estimated by HD<sup>(4)</sup>.

We have now the contrasting conclusions accessible to the experimental discrimination, i.e. (5) from HTT's mechanism and (7) and (10) from HD's mechanism. Our procedure is now to determine  $u_s$  and  $V_d$  severally and hence  $u_s/V_d$  over possibly wide range respectively of  $[OH^-]$ ,  $[Cl^-]$  and  $[I^-]$  to see whether the result is fitted in with by any of the conclusions.

The variation of  $[OH^-]$  is however necessarily accompanied by that of the ionic strength besides the mass effect stated by (5) or (7) and (10). The ionic strength effect is here investigated by observing the effect on  $u_s$  and  $V_d$  of additions of kinetically indifferent salts, i.e.  $NaClO_4$ ,  $NaF$ ,  $CH_3CO_2Na$ ,  $Na_2SO_4$  and  $NaSC_6H_5$ .

### Experimental

A number of runs of experiments were conducted by sealing chloroform air-free together with aqueous alkaline solution of radioactive chloride, of different concentrations of  $OH^-$ ,  $Cl^-$  and  $I^-$ , with or without addition of kinetically indifferent salts in a quartz tube, shaken at  $35^\circ C$  for a recorded time and then chloroform and solution were analyzed to follow the decomposition and chlorine exchange just similarly as in the previous works<sup>(6,7,10)</sup>. The decomposition of chloroform was observed exclusively by titrating chloride ion by the MOHR's method, the chlorine exchange by measuring the radioactivity of solution before the run and that of chloroform after it likewise as in the previous works<sup>(6,10)</sup>, and the hydroxide ion concentration was determined before and after each run by titration with standard sulfuric acid solution.

Hydroxide as well as chloride ion concentration shifts, because of the decomposition of chloroform, more or less with time in every run. Direct observations of runs provide thus time mean  $\bar{V}_d$  of  $V_d$  or of  $u_s$  as given by the equations<sup>\*\*)</sup>

$$\bar{V}_d = \frac{1}{t} \int_0^t V_d dt = \frac{1}{3} \Delta([Cl^-])/t \quad (12. V)$$

<sup>\*)</sup> Mean of the values given in Table II of Ref. 4.

<sup>\*\*)</sup> This equation is based on the fact that three mols of chloride ion are liberated for each mol of chloroform decomposed. Third member of the equation was, in the previous work<sup>(7)</sup>, directly identified with  $V_d$ .

$$\bar{u}_s = \frac{1}{t} \int_0^t u_s dt = - \frac{n^c}{nt} \ln \left( 1 - \frac{\alpha^c C_{1,t}^c v^c n}{\alpha^s C_{1,0}^s v^s n^c} \right)^{**}, \quad (12. u)$$

where  $\Delta[\text{Cl}^-]$  is the increment of chloride ion concentration during the run,  $n^c$  the amount of chlorine in chloroform,  $n$  the total amount of chlorine both in chloroform and in solution,  $v^c$  or  $v^s$  the volume of chloroform or solution present,  $C_{1,t}^c$  or  $C_{1,0}^s$  the directly observed excess count over the background of 1 cc chloroform after the run or of 1 cc solution before it,  $\alpha^c=4.39^{(6)}$  or  $\alpha^s=3.72^{(6)}$  the factor which converts  $C_{1,t}^c$  or  $C_{1,0}^s$  into the respective count, that would be observed in the absence of self-absorption under the particular condition of the present experiment identical with that of the previous determination<sup>(6)</sup> of  $\alpha^c$  and  $\alpha^s$ . The product  $\alpha^c C_{1,t}^c v^c$  or  $\alpha^s C_{1,0}^s v^s$  is now respectively proportional to the number of radioactive chlorine atoms present in chloroform after the run or its constant total number present in chloroform and in solution, and hence  $\alpha^c C_{1,t}^c v^c / \alpha^s C_{1,0}^s v^s n^c$  equals the ratio of atomic fraction  $x^c$  of radioactive chlorine in chloroform to that  $x_\infty$  at the even distribution between chloroform and solution<sup>(6)</sup>, i.e.\*\*\*)

$$x^c/x_\infty = \alpha^c C_{1,t}^c v^c n / \alpha^s C_{1,0}^s v^s n^c. \quad (13)$$

It may be shown that  $\bar{u}_s/\bar{V}_d$  gives the momentary value of  $u_s/V_d$  during the run, which is constant throughout, if  $u_s$  and  $V_d$  are respectively proportional to  $[\text{OH}^-]$ , as

$$\begin{aligned} \bar{u}_s/\bar{V}_d &= \int_0^t u_s dt / \int_0^t V_d dt = k_s \int_0^t [\text{OH}^-] dt / k_d \int_0^t [\text{OH}^-] dt \\ &= k_s [\text{OH}^-] / k_d [\text{OH}^-] = u_s/V_d, \end{aligned} \quad (14)$$

where  $k_s$  or  $k_d$  is the proportionality constant of  $u_s$  or  $V_d$  to  $[\text{OH}^-]$ .

Eq. (12. u) is derived from the equation\*\*\*\*)

$$n^c n^s dx^c/dt = r v^s (n^* - n x^c)$$

shown valid previously<sup>(6)</sup> despite the concurrent decomposition, where  $n^*$  is the total amount of radioactive chlorine in chloroform and solution, and  $n^s$  the total amount of chlorine in solution, radioactive and ordinary. The  $n^c$  decreases during a run by 0.6% at most throughout the present experiment\*\*\*\*), which lies quite within the errors of present determination of  $n^c$ . The above equation is integrated by replacing  $r/[\text{Cl}^-]=r v^s/n^s$  with  $u_s$  and

\*) The third member of this equation equals  $u_s$  according to Eqs. (3.7 S.r), (3.7 S.κ) and (3.8) of Ref. 6, provided that  $n^c$  as well as  $u_s$  is constant during the run, when  $\kappa_s$  of Eq. (3.7 S.κ) of Ref. 6 reduces to unity.

\*\*) Eq. (3.8) of Ref. 6.

\*\*\*) Eq. (3.4) of Ref. 6.

\*\*\*\*) The  $[\text{Cl}^-]$  increases in run 1 by 0.22 mol  $\ell^{-1}$  as seen from Table I, indicating  $0.22 \times 2 \times 10^{-3} \div 3 = 1.5 \times 10^{-4}$  mol chloroform decomposed in 2 cc solution, which amounts to 0.6% of 2 cc or  $n^c=2 \times 1.48/119=0.025$  mol chloroform present.

admitting  $n^c$  thus constant, as

$$\bar{u}_s = \frac{1}{t} \int_1^t u_s dt = \frac{n^c}{t} \int_0^t \frac{dx^c}{n^* - nx^c} = -\frac{n^c}{nt} \ln(1 - x^c/x_\infty),$$

noting  $x_\infty = n^*/n$  by definition and  $x^c = 0$  at  $t=0$ . Eq. (12.  $u$ ) is obtained from the above equation according to (13).

## Results and Conclusions

Table I shows  $\bar{u}_s$ ,  $\bar{V}_d$  and  $\bar{u}_s/\bar{V}_d$  determined at different experimental conditions in comparison with  $u_s/V_d$  calculated by HD's mechanism. The observed ratios  $\bar{u}_s/\bar{V}_d$  are constant around 0.9 almost within *ca.* 30% fluctuations. The ratio appears to increase from that of the first few runs of highest pH to that of runs from 7 to 14 of lower pH and to decrease toward later runs of lower pH but of such high an ionic strength as to equal that of highest pH but these data seem not sufficient further to draw from them any definite conclusion on the correlation between  $u_s/V_d$  and the ionic strength.

Last two columns of Table I show  $u_s/V_d$ -values due to HD's mechanism calculated by (7) on the base of constants (11) for the initial and the final values of  $[\text{OH}^-]$ , between which  $\bar{u}_s/\bar{V}_d$  should lie according to HD's mechanism as deduced from (7). We see from the Table that these values of  $u_s/V_d$  are more than six-folded with decreasing pH while the observed value of  $\bar{u}_s/\bar{V}_d$  remains constant almost within a few ten percent fluctuations in agreement with HTT's mechanism.

Fig. 1 shows the proportionality of  $\bar{V}_d$  to  $[\overline{\text{OH}^-}]$ , i. e.\*)

$$[\overline{\text{OH}^-}] = \frac{[\text{OH}^-]_0 - [\text{OH}^-]_t}{\ln [\text{OH}^-]_0 - \ln [\text{OH}^-]_t} \quad (15)$$

required by (5.b), i. e. by HTT's mechanism, where  $[\text{OH}^-]_0$  or  $[\text{OH}^-]_t$  is the initial or the final value of  $[\text{OH}^-]$ . The proportionality is tolerably

\*) We have for the decomposition in alkaline solution

$$-\frac{d[\text{OH}^-]}{dt} = (3+a)k_d[\text{OH}^-]$$

or by integration,  $[\text{OH}^-] = [\text{OH}^-]_0 \exp\{-k_d(3+a)t\}$ , where  $a$  is the fraction of decomposed chloroform which produces formic acid, and hence

$$[\overline{\text{OH}^-}] = \frac{1}{t} \int_0^t [\text{OH}^-] dt = \frac{[\text{OH}^-]_0 - [\text{OH}^-]_t}{\ln [\text{OH}^-]_0 - \ln [\text{OH}^-]_t}.$$



TABLE I.  $u_s (\equiv r/[Cl^-])$  and

$r$ : Exchange rate of chlorine or the unidirectional rate of  
 $V_d$ : Rate of decomposition of chloroform per unit volume

No. of Runs	Time of Reaction min	Aqueous Solution				Addition of Salt other than Radioactive Chloride mol ℓ <sup>-1</sup>
		Hydrogen Ion Concentration, [OH <sup>-</sup> ] mol ℓ <sup>-1</sup>		Chloride Ion Concentration, [Cl <sup>-</sup> ] mol ℓ <sup>-1</sup>		
		Initial	Final	Initial	Final	
1 <sup>a)</sup>	100	1.615	1.369	0.065	0.284	none
2 <sup>a)</sup>	45	1.236	1.146	0.046	0.155	"
3 <sup>a)</sup>	150	0.942	0.717	0.081	0.281	"
4 <sup>a)</sup>	65	0.892	0.753	0.115	0.230	"
5 <sup>b)</sup>	120	0.443	0.333	0.057	0.144	"
6 <sup>b)</sup>	"	"	"	"	0.139	"
7 <sup>a)</sup>	560	0.0893	0.0363	0.046	0.036	"
8 <sup>a)</sup>	720	0.0352	0.0128	0.110	0.131	"
9 <sup>a)</sup>	"	"	0.0116	"	0.129	"
10 <sup>b)</sup>	1440	0.0342	0.0188	0.074	0.089	"
11 <sup>a)</sup>	720	0.0293	0.0135	0.090	0.106	"
12 <sup>a)</sup>	1440	"	0.0096	"	0.110	"
13 <sup>c)</sup>	"	0.0335	0.0109	0.0113	0.0361	"
14 <sup>c)</sup>	"	"	0.0113	"	0.0505	NaCl 0.0500
15 <sup>c)</sup>	"	"	0.0093	"	0.0482	NaClO <sub>4</sub> "
16 <sup>c)</sup>	"	"	0.0102	"	0.0452*)	NaI "
17 <sup>c)</sup>	"	"	0.0085	"	0.0489	NaF "
18 <sup>c)</sup>	"	"	0.0093	"	0.0506	CH <sub>3</sub> CO <sub>2</sub> Na "
19 <sup>c)</sup>	"	"	0.0072	"	0.0557	NaSC <sub>6</sub> H <sub>5</sub> 0.039
20 <sup>c)</sup>	1000	0.0450	0.0084	0.0110	0.0508	none
21 <sup>c)</sup>	"	"	0.0089	"	0.0488	"
22 <sup>c)</sup>	"	"	0.0150	"	0.041	NaCl 0.571
23 <sup>c)</sup>	"	"	0.0230	"	0.041	" 0.969
24 <sup>c)</sup>	"	"	0.0121	"	0.0446	NaClO <sub>4</sub> 1.003
25 <sup>c)</sup>	"	"	0.0307	"	0.039*)	NaI 0.469
26 <sup>c)</sup>	"	"	0.0108	"	0.0454	NaF 0.424
27 <sup>c)</sup>	"	"	0.0097	"	0.0477	CH <sub>3</sub> CO <sub>2</sub> Na 0.841
28 <sup>c)</sup>	"	"	0.0123	"	0.0474	Na <sub>2</sub> SO <sub>4</sub> 1.177

a): Chloroform 2 cc, solution 2 cc.

b): Chloroform 3 cc, solution 3 cc.

\*) : Sum of chloride and iodide ion concentrations was measured together finally by the as the excess of this value over the sum of initial concentrations of chloride

*On the Mechanism of Decomposition of Chloroform in Aqueous Solution*

$V_d$  at 35°C

chlorine transfer from solution to chloroform per unit volume of solution.  
of solution.

Apparent Specific Radioactivity, Initial, $C_{1,0}^s$ , ct min <sup>-1</sup> cc <sup>-1</sup>	Chloroform	Rates		$u_s / V_d$		
	Apparent Specific Radioactivity, Final, $C_{1,t}^c$ , ct min <sup>-1</sup> cc <sup>-1</sup>	$\bar{V}_d \times 10^6$ , mol l <sup>-1</sup> min <sup>-1</sup>	$\bar{u}_s \times 10^6$ , min <sup>-1</sup>	Observed	Calculated	
				$\bar{u}_s / \bar{V}_d$	Initial	Final
10560	400	730	498	0.68	0.15	0.18
9280	116	807	476	0.54	0.19	0.21
14580	613	443	341	0.77	0.24	0.30
17970	476	592	490	0.83	0.25	0.29
7610	186	241	244	1.01	0.42	0.50
"	159	228	192	0.84	"	"
8450	107	23.0	25.8	1.12	0.87	1.03
19740	132	9.54	11.0	1.15	1.03	1.12
"	120	8.61	10.0	1.16	"	1.13
13940	56	3.43	2.43	0.71	1.04	1.10
17840	96	7.24	9.22	1.27	1.06	1.11
"	107	4.50	4.86	1.08	"	1.10
2480	54	5.72	5.14	0.90	1.04	1.13
"	79	9.06	7.54	0.83	"	1.13
"	82	8.53	7.83	0.92	"	1.14
"	80	7.84	7.63	0.97	"	"
"	83	8.70	7.92	0.92	"	"
"	89	9.08	8.49	0.94	"	"
"	80	10.27	7.64	0.74	"	1.11
"	82	13.3	11.2	0.84	1.00	1.14
"	85	12.6	12.0	0.95	"	"
"	66	10	8.6	0.86	"	1.11
"	35	10	4.4	0.44	"	1.03
"	84	11.2	11.5	1.03	"	1.13
"	33	9	4.5	0.50	"	1.05
"	80	11.5	10.9	0.95	"	1.13
"	61	12.2	8.4	0.75	"	1.14
"	88	12.2	12.1	0.99	"	1.13

c): Chloroform 2 cc, solution 7 cc.

MOHR's method. The increment  $\Delta[\text{Cl}^-]$  of the chloride ion concentration was taken ion and iodide ion. There is given the initial value of  $[\text{Cl}^-]$  plus  $\Delta[\text{Cl}^-]$  thus determined.

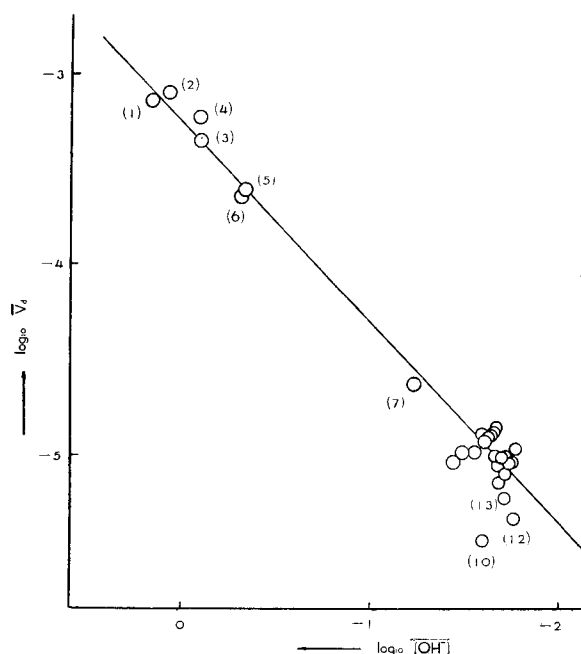


Fig. 1 Plot of  $\log_{10} \bar{V}_d$  vs.  $\log_{10} [\bar{\text{OH}}^-]$ .

obeyed irrespective of the addition of excess chloride or iodide ion, aside from the untraceable fluctuations of a few runs.

In accordance with HD's mechanism,  $u_s$  as well as  $V_d$  must be depressed by the addition of chloride or iodide ion. Let us compare in this regard runs 20 and below, for which  $[\text{OH}^-]_0 = 0.0450$  and  $[\text{Cl}^-]_0 = 0.0110$  commonly. It follows from (10), that  $V_d$  or  $u_s$  varies by the addition of chloride or iodide ion, at constant  $[\text{OH}^-]$ , inversely proportional to  $k_w[\text{H}_2\text{O}] + k_h[\text{OH}^-] + k_{\text{Cl}}[\text{Cl}^-] + k_{\text{I}}[\text{I}^-]$  and hence on the base of constants (11) that  $V_d$  or  $u_s$  of runs 22, 23 and 25 must be diminished respectively by the factor 1.6, 2.0 and 4.5 from that of other runs of this group. Table I shows however  $\bar{V}_d$  of these runs is fairly unaffected by the additions<sup>\*)</sup>, whereas  $\bar{u}_s$  is diminished indeed but much less than HD's mechanism requires.

Experimental results are thus in favour of the HTT's mechanism rather than HD's mechanism.

\*) The  $V_d$  at  $[\text{OH}^-]_0$  i.e.  $V_d = \bar{V}_d [\text{OH}^-]_0 / [\bar{\text{OH}}^-]$  of these runs must be compared, to be exact, with regard to these factors of depression computed for  $[\text{OH}^-]_0$  and  $[\text{Cl}^-]_0$ . The argument is not however altered by the exact comparison.

### Summary

HORIUTI, TANABE and TANAKA (HTT) have arrived at the mechanism of the decomposition and the chlorine exchange of chloroform in aqueous solution, which is at variance with the mechanism proposed by HINE and DOWELL (HD) for the same reactions. The former mechanism requires in alkaline solution, that  $u_s/V_d$  ( $u_s$ : the ratio of the rate of chlorine exchange, i.e. the unidirectional rate of chlorine transfer from solution to chloroform per unit volume of solution over the chloride ion concentration  $[Cl^-]$ ;  $V_d$ : the rate of decomposition of chloroform) and  $V_d/[OH^-]$  are respectively constant independent of concentrations  $[OH^-]$ ,  $[Cl^-]$  and  $[I^-]$  respectively of hydroxide ion, chloride ion and iodide ion within fluctuations expected from the deviation of the mass action law. HD's mechanism requires on the other hand that  $u_s/V_d$  decreases with increasing  $[OH^-]$  and that at constant  $[OH^-]$  both  $u_s$  and  $V_d$  decrease by the same factor by the addition of  $[Cl^-]$  and  $[I^-]$ .

The experiments have shown in favour of HTT's mechanism that  $u_s/V_d$  and  $V_d/[OH^-]$  are respectively tolerably constant irrespective of the excess chloride or iodide ion addition, which deviates from the prediction of HD's mechanism, stated with special reference to the condition of the above experiments, that  $u_s/V_d$  should increase by a factor more than 6 by decreasing  $[OH^-]$ , while both  $u_s$  and  $V_d$  at constant  $[OH^-]$  must be reduced to *ca.* one fifth by the addition of iodide ion.

### References

- 1) J. HINE, R. C. PEEK, JR. and B. D. OAKES, *J. Am. Chem. Soc.* **76**, 827 (1954).
- 2) J. HORIUTI and Y. SAKAMOTO, *Bull. Chem. Soc. Japan* **11**, 627 (1936).
- 3) J. HINE, *J. Am. Chem. Soc.* **72**, 2438 (1950).
- 4) J. HINE and A. M. DOWELL JR., *ibid.* **76**, 2688 (1954).
- 5) J. HORIUTI and K. TANABE, *Proc. Japan Acad.* **27**, 404 (1951); **28**, 130 (1952).
- 6) J. HORIUTI, K. TANABE and K. TANAKA, *this Journal* **3**, 119 (1955).
- 7) J. HORIUTI, K. TANABE and K. TANAKA, *ibid.* **3**, 147 (1955).
- 8) Y. KANEKO and Y. SATO, *this Journal* **6**, 28 (1958).
- 9) A. GEUTHER, *Ann.* **123**, 121 (1862).
- 10) J. HORIUTI and M. KATAYAMA, *this Journal* **6**, 44 (1958).