Title	THE MECHANISM OF THE EXCHANGE REACTION OF CARBON TETRACHLORIDE WITH AQUEOUS CHLORIDE SOLUTION
Author(s)	TANABE, Kozo; ARAMATA, Akiko
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 8(3), 188-196
Issue Date	1960-12
Doc URL	http://hdl.handle.net/2115/24728
Type	bulletin (article)
File Information	8(3)_P188-196.pdf

THE MECHANISM OF THE EXCHANGE REACTION OF CARBON TETRACHLORIDE WITH AQUEOUS CHLORIDE SOLUTION

By

Kozo TANABE and Akiko ARAMATA*)

(Received October 15, 1960)

Abstract

The rate of the chlorine exchange has been measured at 100°C over the whole pH range from 0 to 14. It has been found that the exchange rate was constant independently of hydrogen ion concentration and proportional to chloride ion concentration in solution. The mechanism of the exchange reaction has been determined on the basis of the observed results.

Introduction

We have previously studied the hydrolysis and the chlorine exchange reaction of chloroform and proposed the mechanisms for both the reactions[1][2]. Since no kinetic study has been made of the chlorine exchange of carbon tetrachloride, we have now investigated the exchange reaction.

§ 1. Experimental

Reagents: Carbon tetrachloride of reagent grade was washed with conc. sulfuric acid and distilled water and then fractionally distilled under nitrogen. The radioactive chloride solution of desired pH was prepared by adding dropwise 1.76 N radioactive hydrochloric acid**) into conductivity water, sulfuric acid, sodium hydroxide solution or phosphate buffer solution (2/15 mol/l Na_2HPO_4 + 2/15 mol/l KH_2PO_4). Sodium chloride (guaranteed reagent) was used in experiments for the mass effect of chloride ion concentration on the exchange rate. Conductivity water from an Amberlite resin column was used for making up all solutions for kinetic runs.

Kinetic Runs: Two mℓ of carbon tetrachloride and 1.5, 2.0 or 2.24 mℓ of aqueous radioactive chloride solution of known concentration and of known

---

*) K. T.: Research Institute for Catalysis, Hokkaido University, Sapporo. For inquiries address K. T.
A. A.: Department of Chemistry, Faculty of Science, Hokkaido University.

**) Hydrochloric acid containing Cl^{36} imported from the Atomic Energy Commission, U. S. A.

pH were sealed air-free*) in a quartz tube of 25∼30 mℓ (5 mℓ in an experiment) capacity similarly as in the previous works[1∼4] and the tube was placed in a constant temperature bath**). At a recorded time, the tube was removed, opened, about 1.5 mℓ of carbon tetrachloride carefully pipetted out and washed with conductivity water several times***) and then its radioactivity determined by putting 1 mℓ of the sample in a definite stainless steel tray fitted to a definite G-M counter, as in the previous works[1][3][5].

The radioactivity of the initial solution before the reaction was determined just similarly as that of carbon tetrachloride after the reaction using the above definite apparatusses. The specific radioactivity $\mathbf{C}^S$ (radioactivity in the absence of self-absorption) of the solution and that $\mathbf{C}^C$ of carbon tetrachloride were obtained by multiplying the apparent radioactivity C^S or C^C *i.e.*, the excess count over the background count observed directly by the respective conversion factors particular to the above procedure of measurement. The factor $a^S = \frac{\mathbf{C}^S}{C^S}$ for aqueous solution was determined to be 3.72 in the previous work[1]. The factor $a^{\mathrm{CCl_4}}$ for carbon tetrachloride has been estimated to be 4.71 from the factor $a^{\mathrm{CHCl_3}}$ for chloroform determined previously[1], by assuming that the factor is proportional to specific weight of a material.

The pH of solution was measured at room temperature before and after reaction by means of pH-meter****).

§ 2. Exchange Rate Expression

Carbon tetrachloride exchanges the chlorine with aqueous chloride ion and simultaneously decomposes in aqueous solution. Therefore, chlorine should be transferred forwards from solution to carbon tetrachloride and backwards, the balance of the respective rates being the net rate $\dot{n}^C$ of chlorine increase in carbon tetrachloride, which is practically negative as observed. If r is taken as the forward rate of chlorine transfer for unit volume of solution, the total forward rate is rv^S, the appropriate backward one $rv^S - \dot{n}^C$ and the rate of transfer of radioactive chlorine from solution to carbon tetrachloride $rv^S x^S - (rv^S - \dot{n}^C)x^C$, where v^S is the volume of solution and x^S or x^C is the atomic

---

*) For the procedure of evacuating the tube, see p. 407 of Ref. 3 or p. 84 of Ref. 4.

**) The tube was not shaken, since it has been shown in the subsequent paper[6] that shaking has no effect on the rate of hydrolysis which was about eight hundreds times as large as that of chlorine exchange.

***) The contamination due to radioactive solution was completely eliminated by washing three times.

****) Horiba glass electrode pH meter, Horiba Mfg. Co., Tokyo or Shimadzu glass electrode pH meter, Shimadzu Mfg. Co., Tokyo.

fraction of radioactive chlorine in solution or in carbon tetrachloride respectively. The forward rate r will be called the exchange rate in this paper.

Since the rate of isotopic transfer $rv^S x^S - (rv^S - \dot{n}^C) x^C$ can be expressed by an alternative form $d(n^C x^C)/dt$, where n^C is the amount of chlorine in carbon tetrachloride and t the time of reaction, we have,

$$\frac{d(n^C x^C)}{dt} = rv^S x^S - (rv^S - \dot{n}^C) x^C \tag{1}$$

or

$$n^C \dot{x}^C = rv^S (x^S - x^C) . \tag{2}$$

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

$$n \equiv n^C + n^S \tag{3. a}$$

$$n^* \equiv n^C x^C + n^S x^S , \tag{3. b}$$

where n^S is the quantity of chloride ion in the solution, we have from Eqs. (2) and (3)*),

$$n^C n^S \frac{dx^C}{dt} = rv^S (n^* - n x^C) . \tag{4}$$

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,

$$CCl_3^+ + Cl^- \longrightarrow CCl_4 \tag{5. D}$$

at equilibrium, r or the rate of Eq. (5. D) is constant independently of the activity of chloride ion at constant pH, since the rate of the reversal of Eq. (5. D) which equals r because of the equilibrium is unaffected by the activity of chloride ion.

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

$$Cl^- + CCl_4 \longrightarrow ClCCl_3 + Cl^- \tag{5. S}$$

at 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

$$U_D \equiv r \quad \text{or} \quad U_S \equiv r/[Cl^-] , \qquad (6. D)\ (6. S)$$

namely that r is either constant independently of $[Cl^-]$ or proportional to $[Cl^-]$, Eq. (4) may be integrated as,

---

*) Eqs. (3. a) and (3. b) are referred to hereafter as Eq. (3). This manner of reference will be used in this paper.

$$U_D = \frac{-\log\left(1-\dfrac{x^C}{x_\infty}\right)}{v^S n\displaystyle\int_0^t \frac{dt}{n^S n^C}}, \qquad r \text{ const.}$$

$$U_S = \frac{-\log\left(1-\dfrac{x^C}{x_\infty}\right)}{n\displaystyle\int_0^t \frac{dt}{n^C}}, \qquad r/[\mathrm{Cl}^-] \text{ const.}$$

where $x_\infty = n^*/n$ is x^C at $\dot{x}^C=0$ according to Eq. (4) or the value of x^C attained when radioactive chlorine atoms were distributed evenly between carbon tetrachloride and solution.

Expressing n^C and n^S as $n^C = n_0^C + \dot{n}^C t$ and $n^S = n_0^S - \dot{n}^C t$, the above equations, upon integration assuming $\dot{n}^C$ constant, yield

$$U_D = -\frac{n_0^C n_0^S}{\kappa_D v^S n t}\log\left(1-\frac{x^C}{x_\infty}\right), \tag{7. D}$$

where

$$\kappa_D = \frac{\log\dfrac{1+\dfrac{\dot{n}^C t}{n_0^C}}{1-\dfrac{\dot{n}^C t}{n_0^S}}}{\dot{n}^C\left(\dfrac{1}{n_0^S}+\dfrac{1}{n_0^C}\right)t}$$

or

$$U_S = -\frac{n_0^C}{\kappa_S n t}\log\left(1-\frac{x^C}{x_\infty}\right), \tag{7. S}$$

where

$$\kappa_S = \frac{n_0^C}{\dot{n}^C t}\log\left(1+\frac{\dot{n}^C}{n_0^C}t\right).$$

The x^C/x_∞ in Eq. (7. D) or in Eq. (7. S) may be expressed as,

$$x^C/x_\infty = \frac{a^C C_t^C v^C n}{a^S C_0^S v^S n^C}, \tag{8}$$

where C_t^C or C_0^S is the apparent radioactivity of 1 mℓ carbon tetrachloride at time t or that of 1 mℓ solution at $t=0$ respectively, and a^C or a^S the appropriate conversion factor described in §1, hence $a^C C_t^C v^C$ or $a^S C_0^S v^S$ is proportional to the number of radioactive chlorine atoms present in carbon tetrachloride at time t or the total number present in the reaction vessel respectively.

Both U_D and U_S are calculated according to Eqs. (7) and (8) from the observed values C_t^C, C_0^S etc.

§ 3. Results of Experiment

The results are shown in Table 1. The third column "Aqueous chloride solution" gives the radioactivity of 1 mℓ sample before the reaction directly measured as described in §1 inclusive of background count, the associated background count, pH before or after the reaction measured directly at room temperature, the total quantity of chloride ion before or after the reaction, the volume of solution v^S and the various reagents added. Quantity n_0^S of chloride ion before the reaction was calculated from the specified concentration and the known dilution of the radioactive hydrogen chloride sample mentioned in §1 and from the known amount of added chloride, if any. Quantity n^S after the reaction was the sum of n_0^S and the increment*) $\varDelta n$ of chloride ion formed

TABLE 1. Exchange of Chlorine Labelled by Cl^{36} between

Runs	Time of Reaction min.	Aqueous Chloride Solution						
		Radioactivity before Reaction		pH		Qt. Cl^- ion		Volume v^S mℓ
		Counts/min, mℓ	Background Counts/min	Before	After	n_0^S mmol	n^S mmol	
1	2302	18088	50	0.30	0.25	0.103	0.170	1.5
2	"	18943	"	13.67	13.58	0.107	0.298	"
3	9532	8997	"	0.30	0.10	0.087	0.367	"
4	"	"	"	"	"	1.309	1.590	"
5	"	9611	"	13.67	12.67	0.087	0.506	"
6	"	"	"	"	"	1.290	1.710	"
7*)	"	8997	"	0.30	0.10	0.087	0.367	"
8	4574	17296	"	13.67	13.45	11.80	12.07	2.24
9	"	17472	"	0.30	0.21	12.05	12.23	"
10	"	16472	"	6.73	1.62	0.189	0.411	2.0
11	"	"	"	"	1.30	11.12	11.34	2.24
12	"	15888	"	12.67	1.45	0.239	0.462	2.0
13	"	"	"	"	0.81	11.18	11.40	2.24

*) The volume of vapor phase is less than one twentieth smaller than that in the

---

*) The value were taken from the results obtained in the subsequent paper[6].

during the reaction. The increment was the rate $-\dot{n}^C$ of increase of chloride ion, given in the subsequent column, multiplied by the time of reaction t.

The next column "carbon tetrachloride" shows the directly observed radioactivity of carbon tetrachloride after the reaction, the associated background count, the volume v^C of carbon tetrachloride before the reaction at room temperature and the rate $-\dot{n}^C$ of decrease of chloride ion which was quoted from the results of the hydrolysis in the subsequent paper[6].

The last column "Rates" shows $\log_{10} U_D$ and $\log_{10} U_S$ calculated according to Eq. (7) from the data given in the foregoing columns.

We shall now comment upon the runs of Table 1. The runs 1 to 9 were conducted in strong acidic or alkaline solution (sodium chloride was added in runs 4, 6, 8 and 9). The results are, as shown in the Table, definite exchanges accompanied by slight shifts of pH due to decomposition of carbon tetrachloride. In order to see the exchanges in the mediate pH region, runs 10 and 11 were

Carbon Tetrachloride and Aqueous Chloride at 100°C

	Carbon Tetrachloride					Rates	
Added Reagent	Radioactivity after Reaction		Volume v^C mℓ	Qt. Cl-atom		$\log_{10} U_D$ mol/ℓ, min	$\log_{10} U_S$ min^{-1}
	Counts/min, mℓ	Background Counts/min		n_0^C mmol	Rate of Decrease $-\dot{n}^C/v^S$ mol/ℓ · min		
H_2SO_4	79	55	2	82.84	1.96×10^{-5}	−9.83	−6.05
NaOH	77	"	"	"	2.91×10^{-5}	−9.91	−6.10
H_2SO_4	98	"	"	"	1.96×10^{-5}	−9.96	−6.07
H_2SO_4 +NaCl	91	"	"	"	"	−9.15	−6.15
NaOH	96	"	"	"	2.91×10^{-5}	−9.69	−6.12
NaOH +NaCl	96	"	"	"	"	−9.10	−6.12
H_2SO_4	100	"	"	"	1.96×10^{-5}	−9.81	−6.05
NaOH +NaCl	84	45	"	"	2.91×10^{-5}	−8.46	−6.18
H_2SO_4 +NaCl	72	46	"	"	1.96×10^{-5}	−8.65	−6.36
Buffer	97	67	"	"	7.40×10^{-6}	−10.24	−6.26
Buffer +NaCl	70	52	"	"	"	−8.91	−6.49
NaOH	106	54	"	"	2.91×10^{-5}	−9.81	−6.04
NaOH +NaCl	72	48	"	"	"	−8.65	−6.36

other runs.

conducted in buffer solution and runs 12 and 13 in weak alkaline solution. It was impossible to observe the exchange in narrow range of pH-shift, because of the rapid decomposition which shifts pH off from these regions. Nevertheless, these runs are enough to show the exchange in the mediate pH range.

The chlorine exchange was now investigated with reference to the effects of chloride ion concentration and of the volume of gaseous phase: chloride ion concentration was increased by the addition of sodium chloride in runs 4, 6, 8, 9, 11 and 13 and the volume of vapor phase shortened in run 7 (less than 1/20 of the other runs).

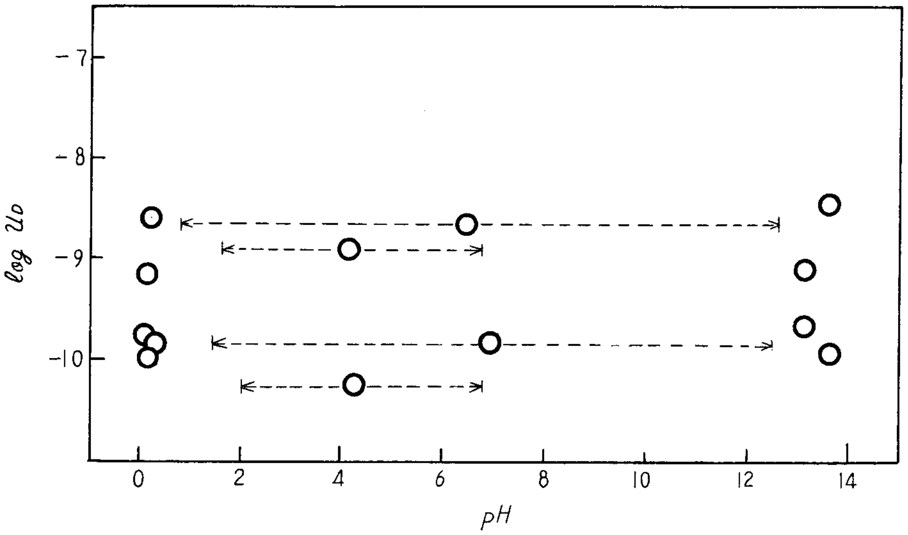

Fig. 1. Rate $U_D \equiv r$ mol Cl/ℓ·min. of chlorine transfer from solution to carbon tetrachloride in one direction, 100°C.
|← →| : Range of pH-variation.

The $\log_{10} U_D$ and $\log_{10} U_S$ are plotted respectively in Figs. 1 and 2 against pH at the middle of range of its variation, if any, during the reaction, shown each by a horizontal dotted line. It is seen from Fig. 1 that U_D varies with $[Cl^-]$ by a factor more than twenty, whereas from Fig. 2 U_S is independent of $[Cl^-]$ as well as of the volume of vapor phase. It is also seen that pH has no appreciable effect on the rate U_S. A straight line is drawn through the observed points in Fig. 2.

It is now concluded from the above results that the exchange rate r is proportional to $[Cl^-]$, the appropriate proportionality factor being independent of $[Cl^-]$, pH and the volume of vapor phase.

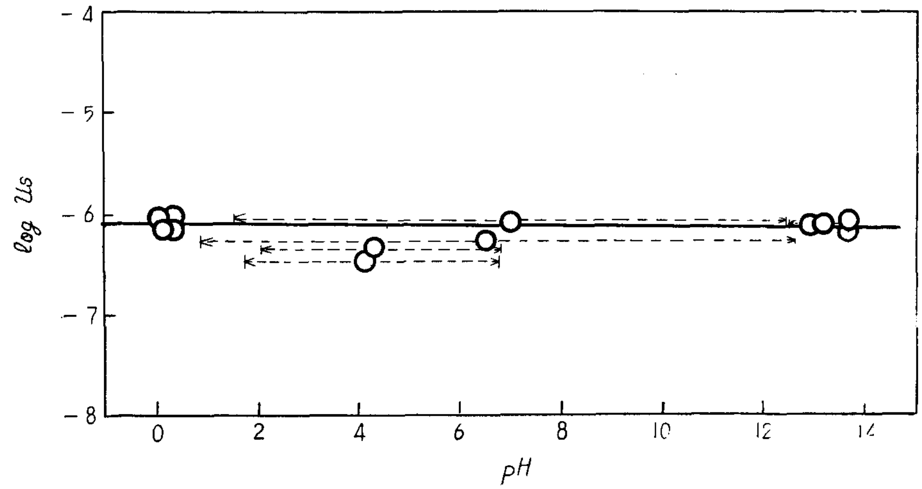

Fig. 2. Specific rate $r/[Cl^-]$ min^{-1}. of chlorine transfer from solution to carbon tetrachloride in one direction, 100°C.
|← →| : Range of pH-variation.

As shown in the subsequent paper[6], shaking has no effect on the rate of the hydrolysis which is about eight hundreds times larger than that of chlorine exchange. It may therefore be admitted that the exchange reaction proceeds homogeneously in the interior of the solution, not being controlled by the dissolution of carbon tetrachloride into solution or its reversal.

§ 4. Discussion

The mechanism of the chlorine exchange will be discussed on the basis of the results in the foregoing section. On the ground of the experimental result that the exchange rate*) is constant independently of pH, we consider the two steps,

$$\text{(I)} \qquad \mathbf{Cl}^- + CCl_3^+ \longrightarrow \mathbf{Cl}CCl_3$$

$$\text{(II)} \qquad \mathbf{Cl}^- + CCl_4 \longrightarrow \mathbf{Cl}CCl_3 + Cl^- ,$$

which are assumed to govern the rate of the chlorine exchange, where **Cl** denotes chlorine atom originating from chloride ion in solution.

The rate-determining step of the decomposition is bimolecular with respect to CCl_4[8] and does not involve chloride ion. It follows that either (I) or (II) which is different from the rate-determining step of the decomposition is practically in equilibrium or that its rates in both the directions are balanced with

---

*) The rate of the transfer of chlorine atom from solution to carbon tetrachloride. Cf. p. 189.

each other, since the decomposition of carbon tetrachloride is the only overall reaction in our assembly.

The exchange rate r must now be constant independently of $[Cl^-]$*) or proportional to $[Cl^-]$ according as (I) or (II) operates. The experimental results in the foregoing section show that r is proportional to $[Cl^-]$. Therefore, the step (II) fits the observed results but the step (I) is ruled out.

It is now concluded that the chlorine exchange proceeds by the step (II) which is in equilibrium.

Acknowledgments

We are indebted to Prof. HORIUTI for a number of discussions on the present work and to Kaisei Association for the grant which made this work possible.

References

1) J. HORIUTI, K. TANABE and K. TANAKA, this Journal **3**, 119 (1955).
2) J. HORIUTI, K. TANABE and K. TANAKA, *ibid.* **3**, 147 (1955).
3) J. HORIUTI and K. TANABE, Proc. Japan Acad. **27**, 404 (1951).
4) K. TANABE and Y. WATANABE, this Journal **7**, 79 (1959).
5) J. HORIUTI and K. TANABE, Proc. Japan Acad. **28**, 127, 130 (1952); **29**, 254 (1953).
6) K. TANABE and A. ARAMATA, this Journal **8**, 197 (1960).
7) J. HORIUTI, *ibid.* **1**, 8 (1948).
8) I. FELLS and E. A. MOELWYN-HUGHES, J. Chem. Soc. 398 (1959).

---

*) The activity of chloride ion was identified with the concentration $[Cl^-]$.