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Instructions for use

60. Photochemical Promotion of Exchange Reaction of Chlorine between Chloroform or Carbon Tetrachloride and Aqueous Chloride Solution

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Introduction

It was reported that the chlorine exchange reaction of chloroform of the project as traced by means of Cl^{36} in dark was rapid when the solution was alkaline but imperceptively slow when acidic even at $100°C$ [*], whereas that of carbon tetrachloride was perceptible at the same temperature neither with alkaline nor with acidic solution [1,2,3].

It has been found now that the irradiation of ultraviolet ray of the spectral range down to 2100 Å upon the above exchange system at room temperature accelerates the exchange of chloroform with the alkaline solution but not perceptively that with the acidic one, whereas it causes considerable exchange of carbon tetrachloride with the acidic solution, leaving however, in contrast to the case of chloroform, that with the alkaline solution imperceptible.

Experimental procedure and the results will be described below.

Experimental

One cc. aqueous radioactive chloride solution and 1.5 cc. chloroform or carbon tetrachloride were sealed together air-free in a quarz tube of 4~6 cc. capacity similarly as in the previous case [1], irradiated by mercury lamp or, in some cases, left for comparison under diffused light or screened from any light by wrapping the sealed tube up with black paper for recorded time at room temperature.

The tube was then opened, 1 cc. chloroform or carbon tetrachloride carefully pipetted out to separate it from the solution and its radioactivity determined just as in the previous case. The sample was then washed with water, if it showed excess count over the background one, and its radioactivity observed again for control of the contamination of radioactive solution.

[*] The present authors have recently observed very small rate of the exchange reaction in the neutral and acidic region. The result will soon be published.

Two mercury lamps were used, one with spectral lines extending down to 3100 Å and the other to 2100 Å as determined by the spectrometer.

The radioactive chloride solution was prepared by diluting properly a portion of 1.029 N HCl containing Cl^{36} of 18 mc./gm. activity supplied by U.S. Atomic Energy Commission. Two samples I and II thus prepared were of 1627 ct./min. cc. and 3264 ct./min.cc. activity respectively inclusive of background count. Their pH was adjusted before use by adding them a proper quantity of H_2SO_4 aq. or NaOH aq.

Chloroform and carbon tetrachloride used in the present experiment are respectively the same preparations used in the previous work[1)2)].

Results

The results obtained with chloroform and carbon tetrachloride are shown in Table I and II respectively. Column 4 in both the

Table I

Cl-Exchange between $CHCl_3$ and Cl^-aq.

Samples : I—1627 ct./min.cc., II—3264 ct./min.cc.

Alkaline :—pH > 9.6   Acidic :—pH < 1.2

1	2	3	4	5		6		7		8
Run	Temp. °C	Time hr.	Irradiation	Solution		$CHCl_3$ activity ct./min.cc.		Background count ct./min.		Color of solution after irradiation
				Sample	pH	Before wash	After wash	Before	After	
1	10	110	Screened	I	Alkaline	62	61	34	33	
2	10	110	Screened	I	Acidic	33	—	34	33	
3	10	110	Diffused light	I	Alkaline	61	61	31	31	
4	10	110	Diffused light	I	Acidic	32	—	32	32	
5	10	110	3100 Å	I	Alkaline	62	61	30	32	
6	10	110	3100 Å	I	Acidic	32	—	32	33	
7	5	11	2100 Å	II	Alkaline	73	70	32	32	Yellow
8	5	11	2100 Å	II	Acidic	32	—	30	32	Slight yellow
9	12	22	2100 Å	I	Alkaline	118 (213)	115 (207)	25	25	Brown
10	12	22	2100 Å	I	Acidic	30	—	29	30	Slight yellow
11	20	146	Screened	I	Alkaline	91	—*	30	30	

* In this case the radioactivity of water used for wash was measured in stead of chloroform to find no excess over the background count.

Table II

Cl-Exchange between CCl_4 and Cl^-aq.

Samples: I—1627 ct./min.cc.,   II—3264 ct./min.cc.

Alkaline:—pH $>$ 9.6   Acidic:—pH $<$ 1.2

1	2	3	4	5		6		7		8
Run	Temp. °C	Time hr.	Irradiation	Solution		CCl_4 activity ct./min.cc.		Background count ct./min.		Color of solution after irradiation
				Sample	pH	Before wash	After wash	Before	After	
1	10	110	Screened	I	Alkaline	33		34	32	
2	10	110	Screened	I	Acidic	34		34	33	
3	10	110	3100 Å	I	Alkaline	31		32	32	
4	10	110	3100 Å	I	Acidic	32		32	33	
5	5	11	2100 Å	II	Alkaline	34		32	32	Slight yellow
6	5	11	2100 Å	II	Acidic	148	145	31	32	Colorless
7	12	22	2100 Å	I	Alkaline	24		23	24	Slight yellow
8	12	22	2100 Å	I	Acidic	177 (333)	176 (331)	25	25	Colorless

cases shows the sort of photochemical treatment i.e. the screening from light by black paper or the exposing to diffused light or that to mercury lamp with spectral range down to 3100 Å or to 2100 Å. Column 3 gives the time of duration of the latter treatment and column 2 the temperature in the mean time. Column 5 shows the sample I or II of the solution and its pH, "Alkaline" and "Acidic" meaning that pH before as well as after the photochemical treatment is respectively either above 9.6, the upper sensitivity limit of the pH test paper set, or below 1.2, the lower one.

Column 6 gives the activity of chloroform or carbon tetrachloride observed directly after opening the tube i.e. before washing with water and that after wash. The figure in the parenthesis shows the excess activity multiplied by the ratio of those of II and I plus background i.e. that expected if II were used instead of I. Column 7 shows the background count observed before and after the measurement of column 6, and column 8 the color of the solution observed after the treatment. Run 11 of Table I is that quoted from the previous result[1] for comparison.

Column 6 both of the tables shows clearly that measured excess of activity is not due to the incomplete separation but to the genuine exchange reaction.

Runs 1, 2, 3, 4, 5 and 6 of Table I show now that diffused light and even the irradiation of the mercury lamp of the range down

to 3100 Å do not influence the exchange both with alkaline and acidic solution, in spite of the fact that the decomposition of chloroform in air is as well known accelerated by sun beam.

Runs 7, 9 and 11 of Table I show now that the exchange is appreciably increased by the irradiation of ultraviolet ray down to 2100 Å with alkaline solution, whereas runs 8 and 10 of the same table that the same irradiation has no perceptible effect with acidic solution.

Runs 1, 2, 3 and 4 of Table II of carbon tetrachloride show that diffused light or ultraviolet ray down to 3100 Å has no effect both with alkaline and acidic solution. It is remarkable that the ultraviolet ray down to 2100 Å causes exchange, as shown clearly by runs 5, 6, 7 and 8, with acidic solution only but not that with alkaline solution, in sharp contrast to the case of chloroform and to the fact that no exchange whatever of carbon tetrachloride has so far been observed in dark[2].

Discussion of Results

It is well known that chloroform and carbon tetrachloride have continuous absorption below 2126 Å and 2300 Å respectively[4]. It might follow from this fact and the present result of spectral range between 3100 Å and 2100 Å being effective that they dissociate, and moreover according to Henrici[4] probably into $CHCl_2 + Cl$ or $CCl_3 + Cl$ respectively. The dissociation of this sort would, however, lead to an exchange reaction, if at all, independent of pH in contradiction to the experiment.

Franck and Ravinowitsch[5] pointed out the "primary recombination effect" in solution i.e. that the molecule which once dissociated having absorbed photon is liable to recombine restoring the normal state on account of collision with the surrounding solvent molecules, unless at least one of the dissociation product is a stable, saturated molecule. This effect might adequately fit in with the observed result, if one attributes to the Brönsted's base or acid AH the part of forming "saturated molecule" with chlorine leading to the exchange reaction and to the solvent molecules the part of suppressing the dissociation of chloroform of the above sort.

Analysis of the dark exchange of hydrogen and chlorine and dark decomposition of chloroform which will be published later, has on the other hand led to the mechanism,

$$CCl_3H + B \longrightarrow CCl_3^- + H^+B \qquad (1.\ a)$$

$$Cl^- + CCl_3^- + HA \longrightarrow ClCCl_2^- + ClH + A^- \qquad (1.\ b)$$
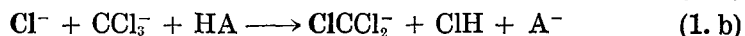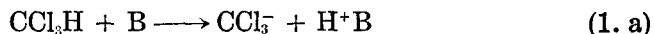
of the two kinds of exchange reaction; (1. a) and its reversal are responsible for the hydrogen exchange, whereas (1. b) and its reversal for the chlorine exchange, the latter determining the rate of the whole process of getting thru the sequence of both the steps.

We might now assume that the photochemical primary process of the chlorine exchange reaction is the step (1. a) accelerated by photon as,

$$CCl_3H + B + h\nu \longrightarrow CCl_3^- + H^+B \qquad (1.\ c)$$
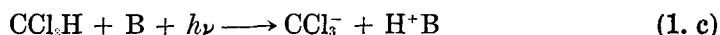
followed by the dark step (1. b). It is inferred now from the fact of (1. b) being the rate-determining that CCl_3^- most probably go back to chloroform by the reversal of (1. a) rather than proceeding with (1. b). This is however due to the dark property of CCl_3^- not depending on light. It may hence be inferred conversely that the dark step (1. b) is, even in the case of photochemical reaction, the rate-determining step i.e., the forward and the backward rates of (1. a) are balanced with each other. It follows now that the light must increase both the forward and backward rates of (1. a) by the same factor n. This means that the activity of CCl_3^- become n times, or that the rate of (1. b) increases by the same factor, or that the light increases the exchange rates of hydrogen and chlorine of chloroform by the same factor. This conclusion will later be thrown to the experimental test in this laboratory.

Exchange reaction of carbon tetrachloride might now be attributed simply to the photochemical process and reversal,

$$CCl_4 + HA + h\nu \longrightarrow CCl_3^+ + ClH + A^- \qquad (2)$$
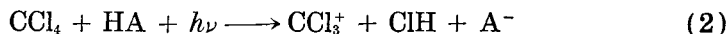
their rates being enhanced in the acidic region of the solution in accordance with the experiment.

It has been expressed in (2) as well as in (1. b), as if the "saturated molecule" involving chlorine atom were a neutral hydrogen chloride molecule throughout, but the possibility can not be excluded that chlorine is released directly in the form of chloride ion under the influence of the positive charge of hydrogen ion.

In the former case when Brönsted's acid inclusive of water molecule is effective, the exchange would proceed at a constant rate at sufficiently high pH. In the latter case the "catalytic" activity is not restricted to the hydrogen ion but more or less shared by any other cation.

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