chlorine and bromine at elevated temperatures to give shorter-chain bromo- and chloro- fluorocarbons. The products are those to be expected from the cleavage of carbon–carbon bonds in the fluorocarbon.

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[A CONTRIBUTION FROM THE INSTITUTE FOR NUCLEAR STUDIES AND THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Exchange of Chlorine Dioxide with Chlorite Ion and with Chlorine in Other Oxidation States

BY HAROLD DODGEN[1] AND HENRY TAUBE

Chlorine dioxide and chlorite ion have, approximately at least, the same configurations, and differ principally only in their charge. It may be expected, therefore, that electron transfer will occur on the close approach of ClO_2 and ClO_2^-. This research was undertaken in the hope of finding evidence for such exchange in aqueous solution, and in the event that the exchange takes place, to study its rate and kinetics. One of these goals has been reached: it has been shown that a rapid exchange does take place in an aqueous solution containing ClO_2 and ClO_2^-, and a lower limit on the specific rate has been set. The research thus far encourages the hope that the rate can be measured quantitatively, and work toward this goal is being continued.

The work has been carried out using the technique, already frequently applied, of mixing a solution containing one of the reaction partners made radioactive with a solution of the other, and observing the rate at which radioactivity is lost from the first partner, or appears in the second. The separation of the partners after exchange was accomplished by extracting the chlorine dioxide from the reaction mixture with carbon tetrachloride. It seems likely that this procedure is unobjectionable, since the properties of ClO_2 are not altered drastically by changing from the solvent water to carbon tetrachloride. However, an actual proof that some exchange is not induced by the method of separation awaits the results of the work on the detailed kinetics.

In addition to offering a simple means for the separation of the exchange partners, the present system also has the important property that any exchange between ClO_2 and ClO_2^- brought about by the operation of the disproportionation equilibrium

$$2ClO_2 + H_2O = ClO_2^- + ClO_3^- + 2H^+$$

may be separately studied, and thus allowed for in considering the direct ClO_2–ClO_2^- exchange. Exchange through this equilibrium may be studied by observing the rate at which activity is transferred between ClO_2 and ClO_3^- in solutions containing these substances.

Experiments have also been carried out to study the exchange of ClO_2 with substances containing chlorine in all the other oxidation stages known to exist in water, namely, ClO_4^-, ClO^-, Cl_2 and Cl^-. It was observed that, with all the oxidation states except ClO_2^-, the rate of exchange is very slow. These results find application in further work using radiochlorine which is to be published later.

Experimental Procedure

The isotope used in this research was Cl^{38}, which decays with a half-life of 37 min., emitting β particles. It was produced by bombarding potassium chlorate with slow neutrons generated in the University of Chicago cyclotron by the impact of 8.5 mev. deuterons on beryllium. Chlorine dioxide was produced by heating a mixtue of 5 g. of bombarded potassium chlorate, 25 g. of oxalic acid and 3 g. of water at 60° in an apparatus similar to that used by Bray.[2] The chlorine dioxide was collected in water after being passed through a solution of 0.5 M in Na_2HPO_4, 1.0 M in NaCl and 0.5 M in $NaClO_3$ to remove any carriers for activity other than chlorine dioxide.

The exchange experiments were performed by mixing an aliquot of the radioactive chlorine dioxide solution with a solution containing the inert chlorine containing species and phosphate buffer or perchloric acid to give the required acidity. After the desired length of time for exchange had elapsed, carbon tetrachloride was added and the chlorine dioxide was extracted.[3] The specific activity was determined by counting the carbon tetrachloride solution in a thin-walled glass cell and measuring the concentration of chlorine dioxide by an iodimetric titration. Throughout this paper the quantity $I_0/100C$ represents the specific activity expressed in arbitrary units. I_0 is the counting rate in counts per minute corrected for decay, and C is the concentration in gram atoms per liter of chlorine in the substance being counted. The specific activity of the chlorine dioxide was determined both before and after contact with the inert chlorine containing species. A decrease in specific activity can take place only if there is exchange of radioactive chlorine dioxide with the other species present, or if non-radioactive chlorine dioxide is produced in the system. The latter process did not occur to a significant extent in any of the experiments performed.

In some of the experiments on the exchange of chlorine dioxide and chlorite the concentration of chlorine dioxide in the solutions counted was too low for analysis, hence the above procedure could not be used for determining the specific activity. These experiments were performed by first running a blank experiment in which a measured volume of inert chlorine dioxide solution of known concentration was added to a measured volume of a solution of the desired activity, then a measured volume of water was added, the mixture stirred and a measured volume of carbon tetrachloride added, the mixture shaken and some of the carbon tetrachloride layer withdrawn and counted.

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(2) Bray, *Z. physik. Chem.*, **54**, 463 (1906).

(3) When chlorine was also present, the chlorine and chlorine exchangeable activity was removed from the carbon tetrachloride layer by extracting with solution containing Cl^- and $HPO_4^{=}$.

In performing an exchange experiment the desired volume of ClO_2^- solution was used in place of an equal volume of water, all other steps being performed as in the blank. This procedure appears to have been satisfactory since there was no evidence of a chemical reaction occurring in the time required to complete the exchange experiment.

In preliminary experiments in which Cl^- and ClO_3^- were omitted from the scrubbing solution it was found that the specific activity of the chlorine dioxide decreased about 10% when left for one minute in the presence of Cl^- or ClO_3^-, and that no appreciable further decrease occurred in eighteen minutes. In addition these samples of chlorine dioxide gave a distribution of radioactivity between water and carbon tetrachloride which was about 20% greater than the chemical distribution ratio, $C_{(CCl_4)}/C_{(H_2O)}$. Evidence that the unknown species of radioactive chlorine was removed by scrubbing with a solution containing 0.5 M Na_2HPO_4, 1.0 M NaCl and 0.5 M $KClO_3$ is presented in Table I. The counting rate in water has been corrected for the difference in counting rate due to change in solvent. The counting rate in water was found to be 1.08 times that in carbon tetrachloride for equal concentrations of radioactive chlorine. The refined chlorine dioxide did not exchange with Cl^- or ClO_3^- (see below) which is further evidence that the unknown species had been removed.

TABLE I

COMPARISONS OF CHEMICAL AND RADIOACTIVITY DISTRIBUTION RATIOS OF REFINED Cl^*O_2, TEMPERATURE 25 ± 2°

Sample	$I_{0(CCl_4)}/I_{0(H_2O)}$	$C_{(CCl_4)}/C_{(H_2O)}$
1	1.72 ± 0.05	1.70
2	1.79 ± .04	1.78
3	1.73 ± .04	1.77

In some experiments, chlorine dioxide of the highest possible specific activity was desired. Some observations on the radioactively impure chlorine dioxide suggested that the initial portions of the gas had a considerably higher specific activity than the later portions. Accordingly, an experiment was performed in which this effect was explored more fully. Successive portions of the chlorine dioxide generated from a single batch of irradiated potassium chlorate were collected in separate portions of carbon tetrachloride. The Cl^- and ClO_3^- exchangeable activity was extracted by washing with solutions containing $HPO_4^=$, Cl^- and ClO_3^-, and the specific activity of the chlorine dioxide left was measured. For the successive portions in order, the specific activities were 435 ± 7, 52 ± 2.3, 40 ± 3, 45 ± 4.4, 41 ± 5. The high initial specific activity can be explained if it is assumed that Cl^*O_2 or perhaps $Cl^*O_2^-$ is produced by the "hot atom" reaction in the crystal. Reactions of this type are known to occur in other crystals.[4]

Even by taking the fullest advantage of the high initial activity, we have been unable to prepare samples of sufficiently high specific activity to permit work at concentrations low enough for accurate measurements of the rate of the ClO_2-ClO_2^- exchange. We are attempting now to prepare chlorine dioxide of sufficiently high activity by exploiting a Szilard-Chalmer's process on CCl_4, then converting Cl^{-*} to $Cl^*O_3^-$, and reducing $Cl^*O_3^-$ to Cl^*O_2.

Results and Discussion

The data obtained on the exchange of chlorine dioxide and chlorine III are presented in Table II.

In columns 5, 6 and 7 are recorded the values of the specific activity before exchange, after exchange, and that calculated for complete exchange, respectively. (This is not the case for the experiments marked "a"; in these the figures represent the actual counting rates, but these are proportional to the specific activities.)

The data show that when the concentrations of ClO_2 and chlorite are about 0.03 M, both in acid and in slightly alkaline solution, the exchange is complete in about six seconds or less. In experiments 2 and 3, the concentrations of ClO_2 and ClO_2^- have been reduced considerably; in both of these there is evidence for incomplete exchange within a period of time of the order of 0.1 min. This effect is particularly striking in experiment 3; experiment 4, which is identical with 3 except that a longer time elapsed before separating, the ClO_2 again shows complete exchange. If the exchange is interpreted as due to the bimolecular processes

$$HClO_2 + ClO_2^* \longrightarrow HCl^*O_2 + ClO_2$$

the specific rates calculated from experiments 2 and 3 for this process are 0.4×10^4 and 1.1×10^4 l. mole^{-1} min.$^{-1}$, respectively. For the present these figures can only be regarded as giving the order of magnitude of a lower limit for the specific rate of the exchange reaction.

Chlorous acid has a dissociation constant[5] at 25° of 4.9×10^{-3} and in the acid solutions used in experiments 1–4, ClO_2^- represents only a small fraction of the total chlorite. Experiment 6 suggests that the exchange rate when most of the Cl(III) is present at ClO_2^- is also measurable. Experiment 8, however, does not present strong indication of incomplete exchange.

The possible errors in the observations arising from failure to reach equilibrium in the extraction

TABLE II

THE EXCHANGE OF ClO_2 AND ClO_2^- IN ACID AND IN SLIGHTLY ALKALINE SOLUTION AT 25 ± 2°

No.	Compositition	(H^+)	t, min.	$I_0/100\ C$ orig.	$I_0/100\ C$ obs.	$I_0/100\ C$ ∞ calcd.
1	0.0306 M $NaClO_2$, 0.0307 M Cl^*O_2 (acid)	1.00	0.1	1007 ± 8	519 ± 12	505 ± 4
2	0.00224 M $KClO_2$, 0.000776 M Cl^*O_2 (acid)	0.6	0.1	7540 ± 100	2280 ± 74	1940 ± 26
3[a]	0.000548 M $KClO_2$, 0.000164 M Cl^*O_2 (acid)	0.5	0.1	247 ± 5	140 ± 6	57 ± 1
4[a]	0.000548 M $KClO_2$, 0.000164 M Cl^*O_2 (acid)	0.5	1.5	247 ± 5	65 ± 7	57 ± 1
5	0.0353 M $NaClO_2$, 0.0354 Cl^*O_2 (phosphate buffer)	6×10^{-8}	0.1	1007 ± 8	519 ± 13	505 ± 4
6[a]	0.000545 M $KClO_2$, 0.000109 M Cl^*O_2	$\sim 10^{-5}$	0.2	145 ± 5	61 ± 4	24 ± 0.8
7[a]	0.000545 M $KClO_2$, 0.000109 M Cl^*O_2	$\sim 10^{-5}$	4.0	142 ± 5	22 ± 4	24 ± 0.8
8[a]	0.000131 M $NaClO_2$, 0.0000447 M Cl^*O_2	$\sim 10^{-5}$	.35	60 ± 3	18 ± 2.5	15 ± 1.0

[a] Actual counting rates (corrected for background) which are proportional to the specific activities are recorded rather than the specific activities.

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(4) Libby, THIS JOURNAL, **62**, 1930 (1940).

(5) Tachiki, *J. Chem. Soc. Japan*, **65**, 346 (1944).

TABLE III

TESTS FOR EXCHANGE BETWEEN ClO_2 AND ClO_4^-, ClO_3^-, ClO^-, Cl_2, Cl^- IN ACID AND SLIGHTLY ALKALINE SOLUTION AT 25 ± 2°

The buffer used was in every case phosphate

No.	Composition	(H^+)	Time in min.	$I_0/100C$ orig.	$I_0/100C$ obs.	$I_0/100C$ ∞
1	0.05 M $KClO_3$, 0.05 M $HClO_4$, 0.0414 M Cl^*O_2	0.05	0.5	196 ± 3	194 ± 5	89[a]
2	0.05 M $KClO_3$, 0.05 M $HClO_4$, 0.0414 M Cl^*O_2	0.05	43	196 ± 3	202 ± 7	89[a]
3	0.05 M $KClO_3$, 0.0414 M Cl^*O_2	6×10^{-8}	0.5	196 ± 3	204 ± 5	89
4	0.05 M $KClO_3$, 0.0414 M Cl^*O_2	6×10^{-8}	48	196 ± 3	189 ± 9	89
5	0.028 M HOCl, 0.028 M NaCl, 0.0313 M Cl^*O_2 (buffer)	6×10^{-8}	0.5	84 ± 2	84 ± 3	30[b]
6	0.028 M HOCl, 0.028 M NaCl, 0.0429 M Cl^*O_2 (buffer)	6×10^{-8}	1	267 ± 3	256 ± 5	116[b]
7	0.028 M HOCl, 0.028 M NaCl, 0.0429 M Cl^*O_2 (buffer)	6×10^{-8}	37	267 ± 3	210 ± 20	116[b]
8	0.039 M HOCl, 0.039 M NaCl, 0.031 M Cl^*O_2 (buffer)	1×10^{-8}	1	612 ± 7	621 ± 9	174[b]
9	0.039 M HOCl, 0.039 M NaCl, 0.031 M Cl^*O_2 (buffer)	1×10^{-7}	24	612 ± 7	579 ± 12	174[b]
10	0.039 M HOCl, 0.039 M NaCl, 0.031 M Cl^*O_2 (buffer)	1×10^{-7}	45	612 ± 7	576 ± 16	174[b]
11	0.0308 M $HOCl^*$, 0.0308 M $NaCl^*$, 0.0223 M ClO_2 (buffer)	6×10^{-7}	1	0	5 ± 4	1030
12	0.0308 M $HOCl^*$, 0.0308 M $NaCl^*$, 0.0223 M ClO_2 (buffer)	6×10^{-7}	32	0	26 ± 13	1030
13	0.0308 M HOCl, 0.0308 M $NaCl^*$, 0.0223 M ClO_2 (buffer)	6×10^{-7}	67	0	50 ± 37	1030
14	0.028 M Cl_2, 0.1 M $HClO_4$, 0.0313 M Cl^*O_2	0.1	0.5	84 ± 2	84 ± 3	30[c]
15	0.028 M Cl_2, 0.06 M HCl, 0.0429 M Cl^*O_2	0.06	1	267 ± 3	268 ± 7	72[d]
16	0.028 M Cl_2, 0.06 M HCl, 0.0429 M Cl^*O_2	0.06	66	267 ± 3	268 ± 7	72[d]
17	0.1 M NaCl, 0.05 M $HClO_4$, 0.0354 M ClO^*_2	0.05	0.5	1007 ± 8	1000 ± 15	263[e]
18	0.1 M NaCl, 0.05 M $HClO_4$, 0.0354 M ClO^*_2	0.05	60	1007 ± 8	1012 ± 22	263[e]
19	0.1 M NaCl, 0.0354 M Cl^*O_2 (buffer)	6×10^{-8}	0.5	1007 ± 8	986 ± 16	263
20	0.1 M NaCl, 0.0354 M Cl^*O_2 (buffer)	6×10^{-8}	55	1007 ± 8	1063 ± 22	263

[a] $I_0/100C$ computed for statistical distribution of radioactivity between ClO_2 and ClO_3^-. [b] For statistical distribution between ClO_2, Cl^- and HOCl. [c] For statistical distribution between ClO_2 and Cl_2. [d] For statistical distribution between ClO_2, Cl_2 and Cl^-. [e] For statistical distribution between ClO_2 and Cl^-.

process, and because of the slight loss of ClO_2 from the stock solution operate in the direction of enhancing the apparent exchange. We are fairly confident therefore that at our highest dilutions the exchange is slow enough to be measurable. Good data on the kinetics of the exchange process can probably be obtained with samples of four or five times the specific activities of the most active samples prepared thus far.

In connection with the observation that charge is readily transferred between ClO_2 and ClO_2^-, it is of interest to note that a reversible potential is established by the ClO_2–ClO_2^- couple in aqueous solution.[6]

Tests for Exchange between ClO_2 and ClO_4^-, ClO_3^-, ClO^-, Cl_2, Cl^-.—The data on the exchange of chlorine dioxide with the other species of chlorine known to be stable in water are presented in Table III. In column 5 is recorded the specific activity of the original chlorine dioxide, in column 6 its specific activity after remaining for the recorded length of time in the solution described, and in the last column the specific activity calculated if the activity were uniformly distributed among all the chlorine atoms present, ClO_4^- in every case excepted.

The results of the experiments reported in Table III show that no appreciable exchange takes place between ClO_2 and the oxidation states ClO_4^-, ClO_3^- and Cl^- in acid or slightly alkaline solution at concentrations of the order of 0.05 M within periods of time up to approximately one hour. That the exchange with ClO_4^- is slow is to be expected, since ClO_4^- is very inert at ordinary temperatures and low acidity. The non-exchange of ClO_2 and ClO_3^- is significant in connection with the observations recorded above for the exchange of ClO_2 and ClO_2^-. In view of the observations made on the ClO_2–ClO_3^- exchange, it can be concluded that no appreciable transfer of activity between ClO_2 and ClO_2^- takes place by way of the equilibrium

$$2ClO_2 + H_2O = 2H^+ + ClO_2^- + ClO_3^-$$

Nothing in the chemistry of Cl^- and ClO_2 suggests that there is a rapid equilibrium which involves these as reactants, and some intermediate oxidation state as product. The experiments on Cl^- and ClO_2 mixtures reported in Table III prove that such an equilibrium does indeed not exist. It is known that Cl^- and ClO_2[7] react, but the rate is appreciable only at higher temperatures and acidity.

Chlorine in acid solution reacts very slowly with chlorine dioxide, and no exchange can be detected in a period of time up to one hour. In neutral solution, chlorine is largely present as hypochlorite and chloride ion. Under these conditions, the rate at which chlorine dioxide is oxidized to chlorate ion is very much greater than in acidic solution. Thus, in the experiments in which the chlorine dioxide and hypochlorite were left together for the longest periods of time (experiments 7, 10 and 13), the chlorine dioxide concentration decreased

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(6) Holst, *Svensk Papperstidn*, **48**, 23 (1945).

(7) Bray, *Z. physik. Chem.*, **54**, 598 (1906).

to about one-half to one-quarter of its original value. The data in the series 6, 7 and 8, 9, 10 indicate some exchange of activity between ClO_2 and hypochlorite. In the series 11, 12, 13, the exchange was followed by noting appearance of activity in ClO_2, rather than the loss from this substance. These data also indicate a slight exchange. The extent of the exchange appears to increase as the extent of the net change in the system increases. Work on this exchange is being continued by H. C. D. and discussion of the mechanism by which exchange takes place is deferred for the present.

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Summary

A rapid exchange between ClO_2 and ClO_2^- takes place in acid and neutral solution (aqueous solutions). At high dilutions (concentrations about 10^{-4} *M*) the rate of exchange is slow enough to be measurable.

ClO_2 does not exchange at an appreciable rate with ClO_4^-, ClO_3^-, Cl_2 or Cl^-. In the presence of HOCl, the oxidation of ClO_2 to ClO_3^- takes place fairly rapidly. In addition to this net chemical change, a slow exchange between HOCl and ClO_2 takes place.

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[Contribution from the Oak Ridge National Laboratory]

A Study of the Effect of a Number of Column Variables[1]

By E. R. Tompkins, D. H. Harris and J. X. Khym

Introduction

In the course of the development of an ion exchange column apparatus for separating and purifying fission products, it became necessary to investigate the effect of a number of operating variables on the efficiency of the column for separating solutes as well as for volume reduction. At the end of the separation step, each fission product is contained in a rather large volume of citrate solution. In most cases it is desirable that the fission product be shipped in hydrochloric acid solution or some other acid which can be removed by distillation. Therefore, it was necessary that this column apparatus not only separate and purify each fission product, but also that one or more volume reduction steps be accomplished and that a metathesis be made so that the final product would be contained in the desired solvent.

In a previous publication of Cohn, Parker and Tompkins,[1a] the principles of the separation and the volume reduction and metathesis steps are discussed. Also shown in this article is a separation column apparatus which was installed in a concrete cell for separating the fission products obtained by exposing uranium in the chain-reacting pile. As pointed out in this publication, the volume reduction and metathesis steps were carried on in a shielded hood after the separation step. Because of the large quantities of fission products which were desired when general distribution of radioisotopes were announced, it was necessary to construct an apparatus which would carry out all of the separation and volume reduction and metathesis steps within the concrete cell, so that it would not be necessary to remove any radioactive substance until the product was removed for shipment.

A tentative engineering design for the apparatus was drawn up, but before the best size and shape for each of the various columns could be decided, it was necessary to determine the factors affecting their efficiencies. It was decided that hydrostatic pressure should be used exclusively to avoid complicating the apparatus. Due to space considerations in the shielded cell in which the equipment was to be built, short columns of large diameter were indicated, in order that the flow rate would not be excessively low. On the other hand, previous experiments[2,3] had shown that the separation efficiency and the volume reduction factor per stage were functions of column length. In determining the geometry of the various columns, it was necessary, therefore, to compromise between the desire for more efficient operation and faster flow rate, since the over-all hydrostatic head for the necessary four stages was limited by the size of the cell in which the apparatus was to be constructed. For this reason the hydrodynamics of column flow and a number of factors determining column efficiency had to be studied so that a reasonable compromise could be made. The first of these studies, made by M. B. Hawkins and R. E. Garber, was described in an Oak Ridge National Laboratory report. The results of the second study are reported here. Also included are the results of a few experiments to test the effect of carrier, both isotopic and non-isotopic, on the efficiency of separations of two similar elements.

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[1] This work was done at Clinton Laboratories (renamed Oak Ridge National Laboratory), a part of the Plutonium Project, during 1945–1946, and was done under Contract W-35-058-eng-71 for the Atomic Energy Project.

[1a] W. E. Cohn, G. W. Parker and E. R. Tompkins, *Nucleonics*, **3**, 22 (1948).

[2] F. H. Spedding, *et al.*, This Journal, **69**, 2786 (1947).

[3] J. X. Khym, E. R. Tompkins and W. E. Cohn, unpublished work.