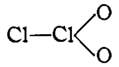
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY AND THE INSTITUTE FOR NUCLEAR STUDIES, UNIVERSITY OF CHICAGO]

Applications of Radioactive Chlorine to the Study of the Mechanisms of Reactions Involving Changes in the Oxidation State of Chlorine

BY HENRY TAUBE AND HAROLD DODGEN

In the chlorine system of oxidation states in water solution representatives of each of the stages between −1 and +7, the +2 and +6 only excepted, are known. Thus each of the substances Cl^-, Cl_2, $ClO^-(HOCl)$, $ClO_2^-(HClO_2)$, ClO_2, ClO_3^- and ClO_4^- persists in water solution and can be well characterized. The reactions of these substances offer a rich field for kinetic investigations and unusual opportunities for reaching a detailed understanding of mechanisms. In this paper is presented an account of experiments which have been done on the mechanisms of some of the reactions using radioactive chlorine as a tracer. The changes studied were oxidation–reduction reactions, and in all cases both the oxidizing and the reducing agents contained chlorine. Experiments have been carried out on the following reactions: (a) the interaction of chlorous acid and chlorate ion, (b) the interaction of chlorine (or hypochlorite) and chlorite, (c) the interaction of chloride ion and chlorate (and the reverse reaction), and (d) the disproportionation of chlorous acid. Included also are experiments on the exchange of chlorine atoms between hypochlorite and chlorite ions and between chlorine and chlorate ion in acid solutions.

Some of the reactions here studied have been investigated kinetically by other workers. While the published data are for the most part incomplete and often conflicting, they are of value in reaching conclusions about the mechanisms of the reactions. In no case do the observations made thus far, including those reported here, suffice to establish mechanisms, but they do in every case lead to significant conclusions. It will be shown that the observations on reactions (b), (c) and (d) require that the activated complex be unsymmetrical in every case, and that the observations for the three reactions can be correlated if an intermediate of the type  $Cl{-}ClO_2$ (or Cl—O—Cl—O) is assumed to be present.

The present paper includes a discussion of earlier work as well as of that performed by us. It is offered as an orienting survey of the reactions in this field, and will be amplified by further experiments. These will include detailed studies of stoichiometry and rates, and will make further applications of isotopes as tracers.

An interesting feature of the reactions in acid solution is that chlorine dioxide is frequently a product. Although not a stable end-product, it persists for long periods of time; both the rate at which it disproportionates and the rate at which it reacts with chlorine in other oxidation states in acid at room temperature are slow. Chlorine dioxide appears in the disproportionation of chlorate in acid, in the reduction of chlorate by chloride ion, the oxidation of chlorite by chlorine or hypochlorous acid and in the disproportionation of chlorite in acid. The feature that chlorine dioxide is present in the system, or that it can readily be generated from some of the substances present, has greatly simplified the work. Chlorine dioxide can readily be separated from other chlorine species using extraction procedures, and most of the tests for radioactivity were therefore made with it. Experiments reported earlier[1] have established the necessary facts about the exchange of activity between chlorine dioxide and chlorine in other oxidation states.

General Experimental Procedures, Conditions, Definitions.—For the tracer experiments the isotope $_{17}Cl^{38}$ was used. It was produced by exposing the appropriate chlorine containing substance to the slow neutron radiation of the University of Chicago cyclotron. For experiments which required the radioactivity to be present in Cl^- or Cl_2, aqueous solutions of hydrogen chloride and of chlorine were exposed. The oxalic acid method previously described was applied in the preparation of Cl^*O_2.[1] A solution containing the chlorine radioactivity as ClO_3^- was prepared by disproportionation of radioactive chlorine in aqueous phosphate buffer at 95°, the chloride ion then being removed by adding silver ion and filtering off the precipitate of silver chloride.

Account of activity was kept in terms of specific activity,[1] $I_0/(100C)$. I_0 is the counting rate expressed in arbitrary units, and C is the concentration expressed as gram atoms per liter of the species containing radioactive chlorine. In all cases solutions in carbon tetrachloride were counted. Chlorine and chloride exchangeable activity were removed from solutions of Cl^*O_2 in carbon tetrachloride by extraction with portions of an aqueous solution 0.5 M in potassium chloride containing also phosphate buffer at a pH above 7. Where activity was present in Cl^-, the specific activity was established by exchanging with chlorine added in known amount, then counting chlorine in carbon tetrachloride and determining the concentration of chlorine in the solutions.

Unless otherwise stated, the temperature at which the experiments were conducted was 25 ± 2°.

The data used in calculating equilibrium constants, with the exception of those for ClO_2^- and

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[1] Dodgen and Taube, THIS JOURNAL, **71**, 2501 (1949).

$HClO_2$, are taken from Latimer "Oxidation Potentials."[2] For ClO_2^- and $HClO_2$ the newer values reported by Fontana and Latimer[3] are used. In all changes involving chlorine dioxide, the values for the equilibrium constants refer to the gas as the standard state for this substance. The value of the coefficient for the distribution of chlorine dioxide[4] between gas and water has been measured in these laboratories. The concentration in solution is 25 times as great as the concentration in the gas phase at 25°.

Results and Discussion

The Reaction: $2H^+ + ClO_2^- + ClO_3^- = H_2O + 2ClO_2$ (g). The present interest in the system ClO_2^-, ClO_3^-, and ClO_2 in acid was to learn something about the rate at which ClO_2^- and ClO_3^- interact in acid. Since the position of equilibrium and the rate of the reverse reaction are pertinent to a consideration of the rate of the forward reaction, a brief discussion of the observations on these aspects of the reaction is presented.

The equilibrium constant for the reaction as represented in the heading is 36. For the net change with $HClO_2$ replacing $H^+ + ClO_2^-$, it is 0.36. These constants show that at equilibrium in neutral solution chlorine dioxide would be almost completely disproportionated, and that even in fairly acid solution the disproportionation would be largely complete. It is known, however that the change is slow except in alkaline solution. For example, a solution in the dark at 0° initially 0.155 M in ClO_2, 0.0011 M in H^+ and also containing the catalyst chloride ion at 0.001 M was observed by Bray[5] to decompose only about 1% in seven weeks. The rate law for the disproportionation in alkali for concentrations of chlorine dioxide in excess of about 10^{-3} M was observed to be[5]

$$-d(ClO_2)/dt = k(ClO_2)^2(OH^-)$$

with the specific rate at 0° equal to 330 $l.^2$ $mole^{-2}$ $min.^{-1}$ and the temperature coefficient 1.81. These data show that disproportionation by this path in acid will be very slow, amounting to only about $10^{-8}\%$ in one hour at 25° for a solution 0.1 M in ClO_2 and 1 M in H^+.

The rate of the forward reaction, $ClO_2^- + ClO_3^-$, has been the subject of considerable discussion. Bray[5] has reviewed the evidence which suggests that the reaction proceeds at an appreciable rate, and has concluded that there is but a single observation which supports this view. This observation[6] is that ClO_3^- enhances the rate at which chlorine dioxide is formed in an acidified solution of chlorite. However, the data reported in his paper indicate no appreciable difference in the rate of decomposition of $HClO_2$ for two solutions in which the concentrations of ClO_3^- are widely different.

The fact that the rate of hydrolysis of chlorine dioxide is very slow in acid, coupled with the fact that the equilibrium constant is about unity requires that the rate at which $HClO_2$ and ClO_3^- react must also be very slow. A direct experimental demonstration, necessary perhaps because the equilibrium constants are probably not very accurate, that ClO_2 and $HClO_2 + ClO_3^-$ do not enter into a rapidly established equilibrium is our observation[1] that no measurable exchange takes place between ClO_2 and ClO_3^- in acid in a period of an hour. An even more direct check has been attempted—to discover whether any of the ClO_2 which forms when ClO_2^- disproportionates in acid in the presence of ClO_3^- is derived from the chlorate ion. This was done by using inert ClO_2^- mixed with radioactive ClO_3^- and testing for the appearance of radioactivity in the product ClO_2.

Experiment.—The initial composition of the reaction mixture of volume 23 cc. was: 0.14 M $Cl^*O_3^-$, 0.037 M chlorite, 0.73 M H_2SO_4 and 0.1 M H_3PO_4. After fifteen minutes had elapsed, during which time about 20% of the chlorite decomposed, 20 cc. of carbon tetrachloride was added and the mixture shaken. The carbon tetrachloride layer was drawn off, and chloride exchangeable activity removed by two successive washings with 5-cc. portions of the chloride + buffer solution. The specific activity of the chlorine dioxide was found to be 0 ± 10. To establish the specific activity of ClO_3^-, the residual chlorite in the water layer was decomposed by acidifying with hydrochloric acid, the chlorine dioxide formed removed with carbon tetrachloride, then $Cl^*O_3^-$ was reduced to Cl^*O_2 by making the solution strongly acid with sulfuric acid. The specific activity of the chlorine dioxide (which will be almost identical with that of chlorate ion—see below) was measured and found to be 2000 ± 61.

This experiment shows that in acid solution, the reaction of $HClO_2$ with ClO_3^- is very much slower than is the disproportionation of $HClO_2$. Under the conditions of our experiments, less than 3% of the chlorine dioxide was formed by the former reaction. If both are second order in the chlorine species, the specific rate of the $HClO_2 + ClO_3^-$ reaction is less than 1/100 that of the $HClO_2 + HClO_2$ reaction. The experiment confirms the conclusion for which other evidence has been cited above, that ClO_3^- and $HClO_2$ even in acid react only very slowly. The contrast in this respect for the system $HClO_2$–ClO_2–ClO_3^- with the analogous one in nitrogen chemistry is striking: HNO_2 is outstanding among ordinary reducing agents for the speed at which it reduces NO_3^-.

The Reaction of Chlorite (ClO_2^- or $HClO_2$) with Chlorine and with Hypochlorite.—Both chlorine dioxide and chlorate ion are products when chlorine reacts with chlorite in acid solu-

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[2] Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

[3] Fontana and Latimer, THIS JOURNAL, **69**, 2598 (1947).

[4] Experiments by John W. Born and Edward F. Gurnee.

[5] Bray, *Z. anorg. allgem. Chem.*, **48**, 217 (1906).

[6] (a) Ref. 5, p. 238; (b) ref. 5, p. 241, *cf.* Expts. 2 and 5 of Table XV.

TABLE I

TEST OF MECHANISM FOR THE OXIDATION BY CHLORINE OF CHLORITE TO CHLORINE DIOXIDE AND CHLORATE ION[a]

Expt.	Reaction	(H^+)	$\frac{I_0}{100C}$ obs.	$\frac{I_0 b}{100C\infty}$	%
1	$Cl_2^* + 2HClO_2 = 2ClO_2 + 2Cl^- + 2H^+$	0.3	7 ± 3	128	6 ± 2
2	$Cl_2^* + 2HClO_2 = 2ClO_2 + 2Cl^- + 2H^+$	0.25	9 ± 3	127	7 ± 2
3	$Cl_2^* + 2HClO_2 = 2ClO_2 + 2Cl^- + 2H^+$	0.30	258 ± 6	4560	5.6 ± 0.1
4	$HCl^*O + 2ClO_2^- = 2ClO_2 + Cl^- + OH^-$	5×10^{-8}	26 ± 11	583	5 ± 2
5	$HCl^*O + 2ClO_2^- = 2ClO_2 + Cl^- + OH^-$	10^{-8}	81 ± 8	1780	4.6 ± 0.5
6	$HCl^*O + ClO_2^- = ClO_3^- + Cl^- + H^+$	10^{-8}	156 ± 10	1780	8.8 ± 0.6

[a] Temperature 25°. Perchloric acid was used in the strongly acidic solutions, phosphate buffer for those of higher *p*H. Calculated for random distribution among the chlorine atoms present as Cl^-, Cl_2, $HClO$, $HClO_2$, ClO_2, ClO_3^-.

tion. In neutral or weakly alkaline solution, the chlorine is largely present as $HClO$ and Cl^-. Under these conditions both ClO_2 and ClO_3^- still appear as products, but the ratio of ClO_3^- to ClO_2 is greater than for acid solutions. Typical observations on the stoichiometry with halogen in excess are the following. In a solution initially 0.4 *M* in perchloric acid, 0.020 *M* chlorine and 0.024 *M* chlorite, 7.8% of the chlorite is oxidized to ClO_3^-, the remainder to ClO_2. In a solution at *p*H about 7.5, with initial $HClO$ at 0.020 *M*, and initial ClO_2^- at 0.024 *M*, 28% of the chlorite is oxidized to chlorate.

The equations expressing the net changes in acid are

$$Cl_2 + 2HClO_2 = 2ClO_2 + 2Cl^- + 2H^+ \quad \Delta F^0 = -6490$$

$$Cl_2 + HClO_2 + H_2O = ClO_3^- + 2Cl^- + 3H^+ \quad \Delta F^0 = -7050$$

and for solutions near the neutral point

$$HOCl + 2ClO_2^- = 2ClO_2 + Cl^- + OH^- \quad \Delta F^0 = -27{,}000$$

$$HOCl + ClO_2^- + OH^- = ClO_3^- + Cl^- + H_2O \quad \Delta F^0 = -31{,}870$$

From the values tabulated for the standard free energy changes, it is evident that equilibrium is far to the right in ordinary acidity ranges for all the changes represented.

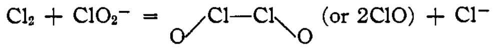
The changes in acid and neutral solutions proceed very rapidly. Chlorine dioxide appears instantly in large amount when the solutions are mixed, and with one of the reactants in excess, the other is consumed almost completely within a minute or so after mixing. In very alkaline solution, however (*e. g.*, 0.1 *M* OH^-), where ClO^- rather than Cl_2 or $HClO$ is the principal species, the reaction is very slow—periods of time of the order of hours being required for appreciable reaction to take place. Nothing appears to have been published on the kinetics of the reactions of chlorine and hypochlorite with chlorite, and in view of the high reaction rates, quantitative work would be difficult.

Two essentially distinct types of mechanism may be considered for this and for similar changes. In one of these, both reactants on primary interaction change to an oxidation state in which they become equivalent, and the intermediate substance thereby produced undergoes further change. In a second type of mechanism, the chlorine atom from the Cl_2 or $HOCl$ at all stages remains distinct from the chlorine atom in ClO_2^-. Experiments making use of radioactive chlorine were undertaken to discover which of these two types operates. A report of these experiments follows.

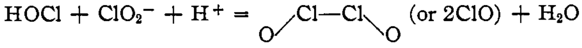
Experiments.—For each experiment a solution containing radioactive chlorine was mixed with a solution containing non-radioactive chlorite. After reaction, the solution was buffered to a *p*H of 7–8 (unless already at that *p*H), carbon tetrachloride was added, the mixture shaken. The carbon tetrachloride layer was then treated as described earlier to measure the specific activity of the chlorine dioxide. The specific activity of the original chlorine was determined on a solution in carbon tetrachloride. Table I summarizes the results of the experiments.

The experiments show that for the most part in the three reactions studied, the atoms present initially in chlorine or hypochlorite appear as chloride ion, and those present in chlorite as chlorine dioxide. A small transfer of activity from chlorine or hypochlorite to the product chlorine dioxide is noted, however, and the effect appears to be real. In experiment 3 of Table I the extractions of the carbon tetrachloride solutions of chlorine dioxide by the aqueous Cl^- buffer solution were continued, the specific activity being measured after each extraction. No change in specific activity was observed —258 ± 6, 257 ± 9, 255 ± 12 — thus proving that the activity was present as chlorine dioxide. The possibility that Cl^*O_2 was formed in the bombardment of chlorine or chloride ion is ruled out on the basis of experiments reported elsewhere.[1] Irradiated chlorine shows no immediate exchange with chlorine dioxide. The relatively high transfer of activity noted in the reaction producing ClO_3^- is probably a result of the procedure followed in the experiment. After reaction, the chlorine dioxide was washed out, and the chlorate ion reduced to chlorine dioxide by adding sulfuric acid. The chloride ion was radioactive and, as is shown below, a slight transfer takes place in the $ClO_3^- + Cl^-$ reaction. The high value for the percentage transfer, 8.8, is probably due to the additional opportunity for exchange in generating chlorine dioxide from chlorate ion in the mixture.

The experiments prove that for the most part at least, the reactions do not proceed by a path in which on primary interaction of chlorine or hypochlorous acid with chlorite a symmetrical intermediate is formed. Thus the mechanisms having as first steps



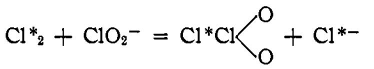
$$\mathrm{Cl_2 + ClO_2^- = {}_{O}\!\diagup Cl{-}Cl \diagdown_{O}\ (or\ 2ClO) + Cl^-}$$



$$\mathrm{HOCl + ClO_2^- + H^+ = {}_{O}\!\diagup Cl{-}Cl \diagdown_{O}\ (or\ 2ClO) + H_2O}$$

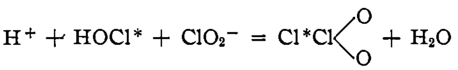
do not account for the major part of the reaction. The principal path must be one in which the chlorine atoms remain distinct, as for example one involving the intermediate $\mathrm{Cl{-}Cl\Big\langle{}^{O}_{O}}$ or Cl—O—Cl—O. There are at present no observations which distinguish the two formulations, and the reactions will be written for the substance $\mathrm{Cl{-}Cl\Big\langle{}^{O}_{O}}$.

Simple steps involving this intermediate which satisfy the observations on stoichiometry and those reported above are



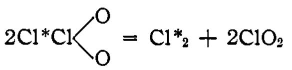
$$\mathrm{Cl^*_2 + ClO_2^- = Cl^*Cl\Big\langle{}^{O}_{O} + Cl^{*-}}$$

or



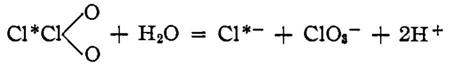
$$\mathrm{H^+ + HOCl^* + ClO_2^- = Cl^*Cl\Big\langle{}^{O}_{O} + H_2O}$$

For the production of ClO_2, the following reaction may be formulated as



$$\mathrm{2Cl^*Cl\Big\langle{}^{O}_{O} = Cl^*_2 + 2ClO_2}$$

and for the production of chlorate ion as



$$\mathrm{Cl^*Cl\Big\langle{}^{O}_{O} + H_2O = Cl^{*-} + ClO_3^- + 2H^+}$$

The slight transfer of activity from Cl^*_2 or HOCl* to the product may result from the oxidation of $\mathrm{Cl^*Cl\Big\langle{}^{O}_{O}}$ to ClO_2 + Cl^*O_2, or from isomerization of $\mathrm{Cl^*Cl\Big\langle{}^{O}_{O}}$ to the symmetrical intermediate.

Test for Exchange in the System ClO^- + ClO_2^-.—An experiment was performed in which radioactive hypochlorite was mixed with chlorite ion in alkaline solution and the substances left in contact for a period of time. The rate of reaction is very slow when (OH^-) is as high as 0.1 *M*. The initial concentrations of ClO^-, ClO_2^- Cl^- and OH^- were 0.0171, 0.0478, 0.0171 and 0.1 *M* in order. At the end of forty-three minutes the solution was acidified, whereupon chlorine dioxide was liberated from the chlorite by hypochlorite. The specific activity of the chlorine dioxide was then measured as described above. It was observed to be 40 ± 13; if the activity had been uniformly distributed among Cl^-, ClO^- and ClO_2^-, the specific activity of the chlorine dioxide would have been 583.

The experiment shows that there was little transfer of activity from ClO^- to ClO_2^-. The slight amount appearing in the chlorine dioxide may be attributed to the transfer in the reaction of Cl^*_2 or HOCl* with ClO_2^- (see above). It may be concluded that the rate of exchange between ClO^- and ClO_2^- is very slow, less than 5% at the concentration above in forty-five minutes. Exchange could conceivably occur by oxygen atom transfer from one group to another. The experiment does not exclude the possibility that such exchange may occur in acid solution.

The System $4H^+ + 2Cl^- + 2ClO_3^- = Cl_{2aq} + 2ClO_2 + 2H_2O$.—The equilibrium constant for this reaction at 25° is 4.7×10^{-7}; thus, appreciable reduction of chlorate ion by chloride ion can be expected only in solutions of high acidity. The forward reaction proceeds fairly rapidly even at room temperature in solutions of high acidity when the concentrations of ClO_3^- and Cl^- are of the order of tenth molar. For example, in 4 *M* $HClO_4$, with ClO_3^- and Cl^- each 0.2 *M*, the color of ClO_2 becomes quite marked in about a minute. In the range of low chloride ion concentrations, the stoichiometry corresponds to that expressed by the equation above. At high chloride ion concentrations, however, relatively more chlorine is formed.

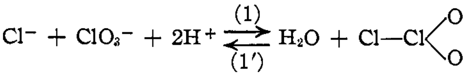
Considerable work on the kinetics of the forward reaction has been reported; much however is conflicting, and none as yet leads to any unambiguous conclusions about mechanism. Among the observations on kinetics which appear well established are the following. The reaction is inhibited by the product chlorine, but not by chlorine dioxide.[7] At low chlorine concentration a limiting rate is reached, and under these conditions the reaction is eighth order[8]

$$-d(ClO_3^-)/dt = k(H^+)^4(Cl^-)^2(ClO_3^-)^2$$

In the presence of iodide ion[9] the reaction reduces to one of simpler order

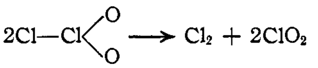
$$-d(ClO_3^-)/dt = k(H^+)^2(Cl^-)(ClO_3^-)$$

Since ClO_2^- and Cl_2 or HOCl are known to react to give ClO_3^- and Cl^- (as well as other products) it may be fruitful to consider the interaction of ClO_3^- and Cl^- in relation to the mechanism suggested for the above reaction. All the observations are consistent with a mechanism of this type formulated in the following way



$$\mathrm{Cl^- + ClO_3^- + 2H^+ \underset{(1')}{\overset{(1)}{\rightleftarrows}} H_2O + Cl{-}Cl\Big\langle{}^{O}_{O}}$$

Equilibrium I
reaction (1) forward
reaction (1′) reverse



$$\mathrm{2Cl{-}Cl\Big\langle{}^{O}_{O} \longrightarrow Cl_2 + 2ClO_2} \qquad (2)$$

Reaction 1 (*i. e.*, I in the forward direction) is the reverse of that written for the formation of chlo-

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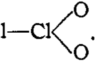
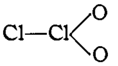
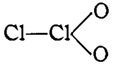
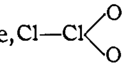
[7] Luther and MacDougall, *Z. physik. Chem.*, **55**, 477 (1906).

[8] Luther and MacDougall, *ibid.*, **62**, 199 (1908).

[9] Bray, *J. Phys. Chem.*, **7**, 112 (1903).

rate in the oxidation of ClO_2^- by Cl_2 or HOCl. It is evident that the pair $Cl^- + ClO_3^-$ can lead to the same intermediate as the pair $HOCl + ClO_2^-$ or $Cl_2 + ClO_2^-$. The mechanism as written leads to the eighth order rate law observed by Luther and MacDougall. The effect of chlorine on the rate may be explained as was done by Luther and MacDougall,[8] or by the assumption that chlorine or HOCl can reoxidize  $\mathrm{Cl{-}Cl}\begin{smallmatrix}\diagup \mathrm{O}\\ \diagdown \mathrm{O}\end{smallmatrix}$. The mechanism is consistent also with Bray's rate law if it be supposed that I^- reacts rapidly with  $\mathrm{Cl{-}Cl}\begin{smallmatrix}\diagup \mathrm{O}\\ \diagdown \mathrm{O}\end{smallmatrix}$ so that the forward reaction in Equilibrium I becomes rate determining. Finally, it may be pointed out that there is no inconsistency in stating that in the present system the substance  $\mathrm{Cl{-}Cl}\begin{smallmatrix}\diagup \mathrm{O}\\ \diagdown \mathrm{O}\end{smallmatrix}$ formed by reaction 1 reverts mainly to ClO_3^- and Cl^- by the reaction 1′ rather than reacting in the second step (this condition is necessary if I is to be maintained as an equilibrium) while in the system $Cl_2 + ClO_2^-$, it reacts principally to form $Cl_2^- + ClO_2$. The reaction $Cl_2 + ClO_2^-$ is much more rapid than is $Cl^- + ClO_3^-$, so that in the former system the steady state concentration of $ClClO_2$ is greater and the 2nd order reaction leading to the products $Cl_2 + ClO_2$ would therefore be favored above the first order reaction of the intermediate to give ClO_3^-.

These considerations show that the observations in the present system may be understood by postulating the same intermediate,  $\mathrm{Cl{-}Cl}\begin{smallmatrix}\diagup \mathrm{O}\\ \diagdown \mathrm{O}\end{smallmatrix}$ (or Cl—O—Cl—O), as was assumed for the reaction of chlorite with chlorine and hypochlorite. As a consequence of this type of mechanism, it would be expected that for the most part, the chlorine atoms in chloride and chlorate would remain distinct on interaction of the two ions, but that a small amount of exchange would occur. An account of the experiments testing this view follows.

Experiments.—Radioactive chloride ion was mixed with inert chlorate in strong acid (4.5 M H_2SO_4), the chlorine dioxide separated, and its specific activity determined as described above. In one experiment, with $(Cl^-)/(ClO_3^-)$, initially at 2, the specific activity of the chlorine dioxide liberated was found to be 7 ± 3; that calculated for random distribution among the chlorine atoms in the system 258. These numbers correspond to 3 ± 1% exchange. In a second experiment, $(Cl^-)/(ClO_3^-)$ was initially 0.5; the observed specific activity of the chlorine dioxide, and that calculated for complete exchange in the products were 8 ± 3 and 135, respectively, corresponding to 6 ± 2% of exchange.

As in the reaction of chlorine or hypochlorite with chlorite ion, the chlorine atoms for the most part remain distinct. Slight exchange is noted, however, about the same in magnitude as was observed for the previous reaction. It seems possible therefore that this small degree of exchange is the property of an intermediate common to both systems.

Only incomplete data on the rate and kinetics of the reverse reaction have been published, but those reported by Bray[10] suffice to show that over a limited range of the ratio $(ClO_2)/(Cl_2)$, the stoichiometry corresponds to that expressed by the equation. His data show, furthermore, that the rate of interaction is slow; thus at 18° in a solution in which ClO_2 and Cl_2 are initially of the order of tenths molar, (H^+) and $(Cl)^-$ 5×10^{-3} M and 2×10^{-3} M, respectively, only a few per cent. of ClO_2 reacts in eight days. Since the equilibrium constant is known, the specific rate and rate law for the forward reaction fix those for the reverse reaction (if the assumption be accepted that the rate law for the reverse reaction will be of the simplest form). The rate law proposed by Bray, similar in form to that found by Sand[11] at higher temperatures and agreeing with data published by Schacherl[12,13] taken together with the equilibrium constant would require a much higher rate for the $Cl_2 + ClO_2$ reaction than was observed by Bray. The observations can, however, be reconciled if the findings by Luther and MacDougall that the forward reaction is inhibited by chlorine is accepted.

An attempt was made to learn something about the rate of the reverse reaction for a system in which the concentrations of reactants and products approach equilibrium values. This was done by introducing radioactive chlorine dioxide into such a system, and observing the change in specific activity with time.

Experiment.—A solution was prepared containing initially 1 M $NaClO_3$, 4.2 M H_2SO_4 and 0.22 M HCl. This remained at room temperature for one day, after which time the concentrations of ClO_2 and Cl_2 were found by analysis to be 0.142 and 0.032 M, respectively. To 13 cc. of this solution was added 10 cc. of a carbon tetrachloride solution 0.098 M in Cl^*O_2 of known specific activity, and 0.074 M in Cl_2. The resulting mixture after shaking was allowed to stand for 86 min. and the specific activity of the chlorine dioxide determined. The results were as follows: the observed final specific activity of the ClO_2 was 81 ± 3, that expected if the only effect were dilution with the inert ClO_2 in the original aqueous solution 89 ± 3; that expected including also complete exchange with ClO_3^-, 19.

The experiment shows that in the time of the experiment, the exchange of chlorine dioxide with chlorate ion is far from complete, and that therefore the rate of reaction of chlorine and chlorine dioxide under the conditions of the experiment is

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[10] Bray, *Z. anorg. allgem. Chem.*, **48**, 228 (1904).

[11] Sand, *Z. physik. Chem.*, **50**, 465 (1906).

[12] Ref. 10, p. 245.

[13] Schacherl, *Ann.*, **182**, 193 (1876).

slow. It should be pointed out that any decrease in specific activity observed sets only an upper limit on the rate of reaction, since adding carbon tetrachloride lowered the concentrations of chlorine and chlorine dioxide, and the net change while probably slight, proceeded in the direction of forming chlorine dioxide from inert chlorate ion. The slow rate observed is not compatible with the rate for the forward reaction far from equilibrium and the equilibrium constant, but is explained if the inhibiting effect of chlorine on the rate of the forward reaction is accepted.

Non-exchange in the System $Cl_2 + ClO_3^-$.—It has been shown that the equilibrium between $ClO_3^- + Cl^-$ and $ClO_2 + Cl_2$ is slow; furthermore, the chlorine atoms originating in ClO_3^- and Cl^- tend to remain distinct. It is also known that chlorine disproportionates to $ClO_3^- + Cl^-$ only slowly in acid. These facts made it seem worthwhile to reinvestigate the exchange between chlorine and chlorate ion in acid, since the rather rapid exchange noted by Libby[14] would therefore seem to imply some mechanism other than these orthodox equilibria for transfer of activity.

A record of the experiment on the exchange of Cl_2 and ClO_3^- is presented in Table II.

TABLE II

EXCHANGE IN THE SYSTEM $Cl_2^* + ClO_3^-$ IN STRONG ACID

($NaClO_3$)	(Cl_2^*)	(H_2SO_4)	Temp., °C.	Time, min.	$I_0/100C$ obsd.	$I_0/100C$ ∞ calcd.
1.0	0.025	2.0	25	1	379 ± 5	18
1	.025	2.0	25	68	375 ± 6	18
0.75	.015	4.5	25	2	300 ± 4	12
.75	.015	4.5	25	61	305 ± 7	12
.75	.015	4.5	25	83	290 ± 9	12
1.0	.0261	3.0	25	2	4250 ± 30	211
1[a]	.0261	3	93	32	3500 ± 150	211
1[a]	.0261	3	93	58	3600 ± 150	211

[a] Heated in sealed tubes.

The experiments were performed by using chlorine solutions of known specific activity, separating chlorine from the reaction mixture at the end of the experiment and determining its specific activity. The data show that at room temperatures there is no significant change in specific activity for periods of time up to approximately one and one-half hours. Even at 93°, the change in specific activity is slight, and probably is for the most part apparent rather than real. At this temperature, about 50% of the chlorine had disappeared at the end of the experiment, and the cell contents were colored slightly yellow. This yellow color was undoubtedly due to chlorine dioxide formed from the chlorate. Since the analysis did not distinguish between Cl_2 and ClO_2, the formation of chlorine dioxide would reduce the apparent specific activity of the chlorine.

The Disproportionation of Chlorite in Acid.—Chlorite is unstable and in acid solution it decomposes fairly rapidly. The principal products of the disproportionation reaction over the whole range of acid concentration in which the rate is appreciable are chlorine dioxide and chlorate ion as higher oxidation states and chloride ion as the lower oxidation state. If the chloride ion concentration remains low, the net change[15] approaches that expressed by the equation

$$4HClO_2 = Cl^- + 2ClO_2 + ClO_3^- + 2H^+ + H_2O$$

However, under most conditions the proportion of chlorate formed is somewhat in excess of that represented above. Small amounts of chlorine are also reported as products.[5] This is surprising in view of the rapid reaction of chlorine and chlorite ion. In an experiment done in this laboratory, differing from Barnett's in that the concentration of acid was much greater (1 M H^+ as compared to a maximum of about 0.2 M H^+ in Barnett's experiments), no measurable amount of chlorine was observed.

Experiment.—The solution was initially 1 M H_2SO_4 and 0.0540 M in total chlorite. After one and one-half hours had elapsed, the chlorine and chlorine dioxide were removed by repeated extraction with carbon tetrachloride. The carbon tetrachloride solution on analysis proved to have no noticeable amount of chlorine. The oxidizing agent which is left in the aqueous solution and which responds to iodide at low acid is chlorite. The chlorate formed is therefore measured by the decrease in total oxidizing power. Perchlorate ion is not a product in this reaction. The concentrations at the end of the time interval were: ClO_2, 0.0171 M; ClO_3^-, 0.0100 M; ClO_2^-, 0.0178 M; Cl_2, 0.000 M.

A study of the kinetics of the decomposition has been made by Barnett. His experiments were for conditions of fairly low acidity ((ClO_2^-) > ($HClO_2$)) and covered a range about twenty-fold in (ClO_2^-) and 3- to 4-fold in ($HClO_2$). The rate law was found to be

$$-d(HClO_2)/dt = k(HClO_2)^2$$

and the value of k at 25°, 1.4 l. mole^{-1} min.$^{-1}$.

Chloride ion catalyzes the disproportionation of $HClO_2$, and changes the stoichiometry of the reaction. Thus, in an experiment in which the solution was initially 0.472 M HCl and 0.0280 M $NaClO_2$, after eight minutes had elapsed, the total chlorite had fallen to 0.0149 M, and the concentrations of the products ClO_2 and ClO_3^- were 0.0091 and 0.0012 M, respectively. The fraction of the chlorite ion appearing as chlorate ion is much less in the chloride catalyzed reaction than it is in the uncatalyzed change.

The observations may all be understood on the basis that in the uncatalyzed reaction, the primary step is

$$2HClO_2 \longrightarrow HClO + H^+ + ClO_3^-$$

and in the catalyzed reaction

$$HClO_2 + Cl^- + H^+ \longrightarrow 2HClO$$

The oxidation of chlorite by HClO or chlorine as

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[14] Libby, THIS JOURNAL, 62, 1930 (1940).

[15] Barnett, Thesis, University of California, 1935.

follow reaction yields mainly chlorine dioxide and accounts for the observed stoichiometry.

We have performed experiments to establish whether for the catalyzed reaction the chlorine atoms in the chloride ion remain distinct from those appearing in the product ClO_2. On the basis of the mechanism proposed above for the change, it is expected that they do remain distinct, since very little transfer of activity from HCl^*O or Cl_2^* to ClO_2 takes place in the reaction of these with ClO_2^-.

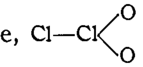
The experiments are outlined below, and show that in fact little mixing of activity between Cl^- and ClO_2^- is observed when the former acts as catalyst for the disproportionation of chlorite ion. The slight amount of exchange, about the same in extent as in the oxidation of chlorite by chlorine or hypochlorite, supports the view that the same intermediate is involved in both reactions.

Experiment.—The concentration of hydrochloride in each experiment was 0.58 *M*. The chloride ion was radioactive and its specific activity was determined before the reaction. After considerable chlorine dioxide had been formed, it was separated from other species as described above, and its specific activity determined. In one of the experiments, the specific activity of the chlorine dioxide formed was 4 ± 4, that expected if exchange with the halogen in the system were complete 50; in a second, these numbers were 27 ± 15 and 336. The results in the second experiment correspond to 8 ± 5% exchange. Thus the amount of exchange which takes place is about the same as in the oxidation of chlorite by chlorine or HOCl. Since the mechanism proposed includes as a step the oxidation of chlorite by HOCl or chlorine, slight transfer of activity to the product ClO_2 is expected.

Acknowledgment.—The cyclotron was operated with the aid of funds from the Office of Naval Research (N60NR-20, Task Order III). The authors wish to express their appreciation also to Joseph Halperin for help with some of the experiments.

Summary

By experiments using radioactive chlorine as a tracer, the following observations have been made. (a) The oxidation of chlorite by chlorate in acid is much slower than the disproportionation of chlorite. (b) In the reaction of chlorite with chlorine (or hypochlorous acid) to form chlorine dioxide or chlorate and chloride ion, most of the chlorine atoms in the chlorine dioxide or chlorate are derived from the chlorite. (c) In the reaction of chloride ion with chlorate ion in acid to produce chlorine and chlorine dioxide, the chlorine atoms in the chlorine dioxide are for the most part derived from the chlorate. (d) In the disproportionation of chlorite in acid catalyzed by chloride ion, the chlorine atoms in the chlorine dioxide are for the most part derived from the chlorite. (e) In each of the changes under (b), (c) and (d), a small but definite degree of mixing of the chlorine atoms in the products has taken place. (f) The reverse reaction in the system (c) near its equilibrium composition is very slow. (g) The exchange of chlorine activity between ClO^- and ClO_2^- in base is very slow. (h) The exchange of chlorine with chlorate ion in acid at room temperature and at elevated temperatures is very slow.

The significance of these observations in relation to other published observations and in relation to reasonable mechanisms for the reactions has been discussed. An unsymmetrical intermediate,  $\mathrm{Cl{-}Cl}{<}^{\mathrm{O}}_{\mathrm{O}}$ (or Cl—O—Cl—O), common to the systems (b), (c) and (d) is postulated.

CHICAGO, ILLINOIS RECEIVED JANUARY 14, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FRESNO STATE COLLEGE]

The Apparent and Partial Molal Volume of Copper Sulfamate in Aqueous Solutions

BY ELTON M. BAKER

The object of this investigation was to determine the apparent and partial molal volume of copper sulfamate at 25° for various concentrations of solutions from accurate density measurements. At infinite dilution the apparent molal volume becomes the partial molal volume. The literature contains limited data for salts of the type contained in this study.

Experimental

The experimental procedure consisted of determining densities of aqueous solutions of copper sulfamate in calibrated weld precision pycnometers of approximately 25 ml. capacity. These were calibrated using distilled water. The deviation was less than 0.005%. The density obtained for each concentration is the average of three determinations. The maximum deviation between values in any series was 0.005%. The densities were determined at 25 ± 0.02°. The temperatures were determined by a long mercurial thermometer of short range, calibrated by the National Bureau of Standards. Calibrated weights were used and weighings could be reproduced to ±0.05 mg. All weights were corrected to vacuum. Weighing was done in a room at 25 ± 1°.

Copper sulfamate was prepared by the interaction of C. P. sulfamic acid and basic copper carbonate. The blue copper sulfamate was recrystallized three times from distilled water. The copper content was determined by allowing an excess of potassium iodide to reduce weighed samples of the stock solution of copper sulfamate in an acid buffer. The released iodine was titrated using standard thiosulfate solution with potassium thiocyanate added