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The Rapid Interaction between Sodium Chlorite and Dissolved Chlorine[1]

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The reactions

$$2HClO_2 + HClO \longrightarrow 2ClO_2 + Cl^- + H_2O + H^+ \quad (1)$$

$$2HClO_2 + Cl_2 \longrightarrow 2ClO_2 + 2Cl^- + 2H^+ \quad (2)$$

are interesting not only by themselves but in that they may play a key role in the oxidation reactions of metal ions by chlorine-containing oxidizing agents.[2-5] Reactions 1 and 2 have been found inevitably to be accompanied by reactions which lead to the formation of ClO_3^-, for example

$$HClO + HClO_2 \longrightarrow ClO_3^- + Cl^- + 2H^+ \quad (3)$$

We have observed that the lower the concentration of $HClO_2$, the more ClO_3^- that is produced. However, the addition of the product ClO_3^- has little or no influence on the over-all course of reaction 1, 2, or 3.

When $HClO_2$ is oxidized by dissolved Cl_2, less ClO_3^- is formed than when HOCl is the oxidizing agent (*i.e.*, the stoichiometry approaches that given by reaction 2). Reaction 2 is considerably faster than reaction 1.

Kinetic studies on both reactions 1 and 2 which are indeed rapid are complicated by the fact that of all the species involved, only ClO_2 can be conveniently determined. This fact coupled with the concentration dependence of the stoichiometry allows only qualitative observations to be reported at this time. It should be pointed out that these qualitative observations themselves are sufficient to provide verification for the model used to understand the mechanism for the production of chlorate in the uranium(IV)–chlorite[2a,3] and in the vanadium(II)–chlorite reactions.[4]

Experimental Section

All the chemicals and analytical procedures used for this study have been described elsewhere.[2b,4] The concentration of dissolved chlorine dioxide was measured spectrophotometrically. The molar absorbance was calculated to be 1240 M^{-1} cm^{-1} at 360 mμ.[5] The rate of formation of dissolved chlorine dioxide was followed by means of the rapid mixing apparatus described by Thompson and Gordon.[6]

Three different procedures were used to initiate the reaction between sodium chlorite and the oxidizing agents used (dissolved chlorine or hypochlorite). The first procedure involved the rapid acidification of a slightly basic mixture of sodium chlorite and sodium hypochlorite by the addition of perchloric acid of the appropriate concentration. The second procedure involved the rapid addition of aqueous sodium chlorite to an acidic solution of hypochlorous acid. The third procedure involved the addition of aqueous sodium chlorite to an acidic solution of dissolved chlorine. In all cases, a 2-cm spectrophotometer cell was stoppered with a rubber serum cap, and the reagent was added by means of the rapid mixing syringe which has been shown to have a mixing time of 30 msec.[6]

Results and Discussion

The reaction between sodium chlorite[7] and hypochlorous acid has been discussed by Taube and Dodgen.[8] The results of our study of the stoichiometry of reaction 1 and the subsequent formation of chlorate are shown in Table I.

TABLE I

THE REACTION BETWEEN SODIUM CHLORITE AND HYPOCHLOROUS ACID[a]

10^4[NaOCl), *M*	10^4[$NaClO_2$], *M*	10^4[ClO_2][b] produced, *M*
15.0	6.0	2.5 ± 0.1[c]
7.5	3.0	0.60 ± 0.10[c]
3.0	3.0	0.49 ± 0.09[c]
1.5	3.0	0.42 ± 0.08[c]
1.5	6.0	2.4 ± 0.05[c]
1.5	15.0	3.8 ± 0.04[c]
1.5	30.0	4.3 ± 0.04[c]
...	30.0	0.03[e]
15.0	3.0	0.84 ± 0.03[d]
7.5	3.0	1.1 ± 0.1[d]
3.0	3.0	1.4 ± 0.1[d]
1.5	6.0	2.8 ± 0.1[d]
1.5	15.0	3.5 ± 0.1[d]

[a] Final acidity was 0.20 *M* $HClO_4$. [b] Each data point is the average of several experiments and the errors are deviations from the mean. [c] Rapid acidification of basic mixture of sodium chlorite and sodium hypochlorite. [d] Rapid addition of aqueous sodium chlorite to an acidic solution of hypochlorous acid. [e] Acidification of sodium chlorite in the absence of other oxidizing agents such as chlorine. Result reported after 20 sec. After 5 min only 1.25×10^{-4} *M* ClO_2 was produced. For additional results of the disproportionation of chlorous acid see the work of Kieffer.[5]

These data show that there is a marked influence on the stoichiometry as the amount of excess oxidizing agent is changed. However, as soon as sodium chlorite is in excess, the production of chlorine dioxide markedly improves. Actually, the theoretical amount predicted by eq 1 is exceeded, which perhaps can be explained by a chlorine or hypochlorous acid catalysis of the disproportionation of sodium chlorite. The difference in yield of chlorine dioxide as the method of mixing is changed suggests that the chlorite–hypochlorite or

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[1] This research was supported in part by Grant No. 14-0001-01-405 from the Office of Saline Water.

[2] (a) G. Gordon and F. Feldman, *Inorg. Chem.*, **3**, 1728 (1964); (b) R. C. Thompson and G. Gordon, *ibid.*, **5**, 562 (1966).

[3] G. Gordon and D. M. H. Kern, "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., Pergamon Press, New York, N. Y., 1964, pp 655–660.

[4] G. Gordon and P. H. Tewari, *J. Phys. Chem.*, **70**, 200 (1966).

[5] R. G. Kieffer, Ph.D. Thesis, University of Maryland, 1966.

[6] R. Thompson and G. Gordon, *J. Sci. Instr.*, **41**, 480 (1964).

[7] No attempt will be made to differentiate between ClO_2^- and $HClO_2$, although, under the conditions of experiments reported here, the predominant species is $HClO_2$.

[8] H. Taube and H. Dodgen, *J. Am. Chem. Soc.*, **71**, 3330 (1949).

chlorite–chlorine reaction is competitive with the chlorine–hypochlorite equilibrium.[9]

Increased concentrations of the reactants result in proportionately more chlorine dioxide. These results are shown in Table II; for the more concentrated solutions, the amount of chlorate in the final solution was determined titrimetrically. For the more dilute solutions, the difference between the total oxidizing power and the chlorine dioxide was assumed to be due to chlorate.

TABLE II

RAPID ADDITION OF SODIUM CHLORITE TO AQUEOUS CHLORINE[a]

Initial $[NaClO_2]$, *M*	Oxidizing power found	
	% ClO_2	% ClO_3^-
10^{-2}	90	10
3×10^{-3}	82	18
3×10^{-4}	54	46
10^{-4}	30	70
10^{-5}	<10	>90

[a] 0.2 *M* $HClO_4$ with 2:1 molar ratio of $NaClO_2$ to Cl_2.

For all of the reactions reported in Tables I and II, the production of chlorine dioxide is very rapid and is over in less than 1 or 2 sec. After the reaction is completed, no change in absorbance occurs. Therefore, it was concluded that chlorate does not result from the disproportionation or further oxidation of dissolved chlorine dioxide, but the chlorate must be produced by a reaction concurrent with reaction 1. The reaction for the production of chlorate must be of lower order than reaction 1 because its rate is less affected by dilution, which results in the production of relatively larger amounts of chlorate in the more dilute solution.

In the presence of excess initial chloride, the hypochlorous acid preferentially reacts with chloride ion to form chlorine[9] which then oxidizes the sodium chlorite. We have shown that the reaction between sodium chlorite and dissolved chlorine is more rapid than the chlorite–hypochlorous acid reaction. However, the same type of stoichiometric complications are observed.

The rate of production of dissolved chlorine dioxide as given by eq 1 and 2 has been followed spectrophotometrically as a function of time. The most convenient experimental conditions were such that only 60% of the maximum amount of chlorine dioxide was produced. In roughly 0.01 *M* solutions, approximately 10% chlorate is formed. However, this results in such rapid rates of production of chlorine dioxide that it is difficult to follow the reaction completely with our mixing apparatus, even at 0°. Typical results for the half-life of the chlorite–hypochlorous acid reaction are shown in Table III.

TABLE III

HALF-LIVES[a] FOR THE REACTION BETWEEN SODIUM CHLORITE AND HYPOCHLOROUS ACID IN 0.20 *M* $HClO_4$

$[HClO_2]$, *M*	$[HOCl]$, *M*	Temp, °C	% ClO_2[b]	$t_{1/2}$, sec[c]
2.9×10^{-4}	2.9×10^{-4}	23	61 ± 2	3.5 ± 0.1
0.9×10^{-3}	0.9×10^{-2}	11	60 ± 2	0.08 ± 0.01
0.9×10^{-3}	0.9×10^{-2}	1.0	73 ± 3	0.15 ± 0.01
5.5×10^{-4}	1.5×10^{-4}	11	93 ± 3	6.2 ± 0.1
1.8×10^{-2}	1.5×10^{-4}	23	125 ± 4	0.84 ± 0.01

[a] Average values are reported and the errors correspond to deviations from the mean. [b] Based on eq 1. [c] Time needed to produce half of the amount of chlorine dioxide produced.

If the data in Table III are converted to the appropriate rate constants and the reaction order is calculated by means of the Noyes equation,[10] this results in an over-all reaction order of 1.93 ± 0.10. Agreement between individually calculated rate constants is somewhat poor but better than the assumptions of first or third order for the over-all reactions. Some of these complications are probably caused by the formation of dissolved chlorine due to the reaction between hypochlorous acid and chloride ion. Therefore, the study of the oxidation of sodium chlorite by dissolved chlorine was also undertaken in an attempt to establish this point. The stoichiometry for the reaction was assumed to be that shown in eq 1.

The reaction order for the chlorite–chlorine reaction was calculated by means of the Noyes equation,[10] and it was found to be 2.1 ± 0.1. The best agreement between different runs was obtained with the assumption of an over-all second-order reaction. Typical results are shown in Table IV. It should be pointed out that the experiments shown in Table IV are somewhat complicated in that the chloride ion was necessarily in excess. Thus it is possible that part of the difference between the rate with hypochlorous acid and chlorine could be due to an additional path which is catalyzed by chloride ion.

TABLE IV

HALF-LIVES[a] FOR THE REACTION BETWEEN SODIUM CHLORITE AND DISSOLVED CHLORINE IN 0.8 *M* $HClO_4$ AT 23° WITH 0.1 *M* NaCl

$[ClO_2^-]$, *M*	$[Cl_2]$, *M*	% ClO_2	$t_{1/2}$, sec[a,b]
2.54×10^{-3}	1.27×10^{-3}	96 ± 1	0.03 ± 0.002
1.27×10^{-3}	0.64×10^{-3}	89 ± 2	0.06 ± 0.003
1.27×10^{-3}	1.27×10^{-3}	93 ± 2	0.063 ± 0.002

[a] Average values are reported and the errors correspond to deviations from the mean. [b] Time needed to produce half of the amount of chlorine dioxide produced.

A mechanism consistent with these stoichiometric and kinetic observations is similar to that proposed by Taube and Dodgen.[8] The proposed mechanism suggests a different path for chlorine and hypochlorous acid which is consistent with data presented in Tables I–III.

$$Cl_2 + ClO_2^- \longrightarrow Cl^- + [Cl_2O_2] \qquad (4)$$

$$HOCl + HClO_2 \longrightarrow H_2O + [Cl_2O_2] \qquad (5)$$

followed by, in dilute solution

$$[Cl_2O_2] \longrightarrow Cl^- + ClO_3^- \qquad (6)$$

and in more concentrated solutions by

$$2[Cl_2O_2] \longrightarrow Cl_2 + 2ClO_2 \qquad (7)$$

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(9) M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, **84**, 1355 (1962).

(10) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 41.

Although reactions 6 and 7 may not be rate determining, they must determine the final ratio of chlorine dioxide to chlorate ion. The rate of formation of the intermediate (Cl_2O_2) would be over-all second order; reaction 6 would necessarily be first order, and reaction 7 must be second order. At higher pH values, these reactions appear to be considerably slower. This would account for the production of primarily chlorate ion in dilute solution with the yield of chlorine dioxide increasing as the over-all reactant concentration increased.

In conclusion, we have shown that chlorine oxidizes chlorous acid more rapidly than does hypochlorous acid and, in dilute solution, the primary product is chlorate ion but that, in more concentrated solutions, the main product is chlorine dioxide. The suggested intermediate (Cl_2O_2) is somewhat analogous to the stable and well-defined compound ClO_2F. These results would also account for the formation of chlorate when chlorite is used to oxidize metal ions such as uranium(IV)[2a] or vanadium(II),[4] in that the corresponding metal ion-hypochlorous acid reactions are slow as compared to the hypochlorous acid-chlorous acid reaction, and at most only very low concentrations of Cl_2O_2 would result. The major product should indeed be chlorate ion and not chlorine dioxide.

Correspondence

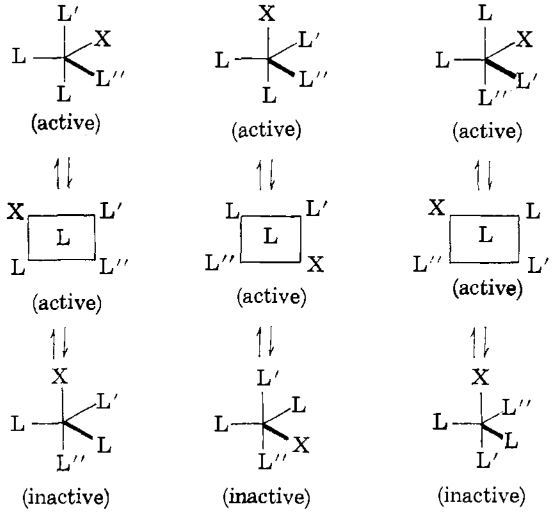
Intramolecular Racemization Processes in Pentacoordinate Structures

Sir:

In a recent review[1] and also in earlier articles,[2-4] brief mention was made of intramolecular racemization processes in optically active pentacoordinate structures. These processes were characterized in general as facile rearrangements based on interconversions of trigonal-bipyramidal and tetragonal-pyramidal geometries. *Within the context of this specific mechanism first delineated by Berry,*[5] the various classes[1] of pentacoordinate structures are assayed in this note for feasibility and ease of racemization only.[6]

XMLL′L″L‴.—With five nonequivalent unidentate ligands, neither the trigonal-bipyramid nor the tetragonal-pyramid model possesses a plane of symmetry.[7] Intramolecular racemization of an optically active XMLL′L″L‴ species can be achieved in plane-pentagonal geometry but the latter state should be very high in energy and should be preempted by the more energetically attractive racemization process comprising ligand dissociation.[8] Alternatively, racemization may be achieved in an idealized process involving the trigonal bipyramid ⇄ tetragonal pyramid intramolecular rearrangement which comprises as a minimum a tenth-order[9] process. An exemplary compound for experimental evaluation of these assessments is $R_1R_2R_3PClF$ because the pronounced affinity of alkyl and aryl groups (relative to halogen atoms) for equatorial sites should yield relatively long-lived ground-state geometries.

$XML_2L'L''$.—With this kind of substitution, there are seven possible isomers in trigonal-bipyramidal geometry of which four isomers have a plane of symmetry. The three asymmetric isomers have in common an equatorial and an axial L ligand. Racemization



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[1] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

[2] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

[3] E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

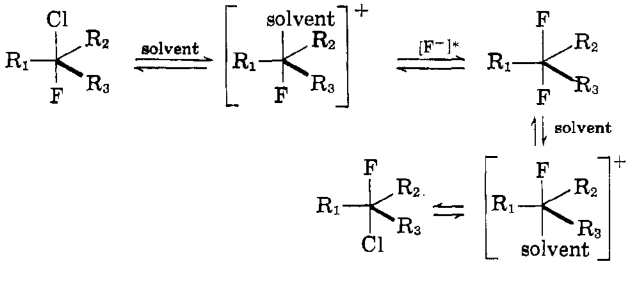
[4] E. L. Muetterties, *ibid.*, **4**, 769 (1965).

[5] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

[6] Only structures with asymmetry originating at the central atom are evaluated here.

[7] Absence of any planes of symmetry is not, of course, sufficient to define a geometry that has *d* and *l* isomers. The precise statement for the conditions necessary for optical activity is given in H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, New York, N. Y., 1957, p 346.

[8] Racemization may occur through a dissociative route in the following manner



or by conversion to an octahedral intermediate or transition state through F^- addition. *$[F^-]$ may be derived directly or indirectly from $R_1R_2R_3PClF$.

[9] Order is defined by the number of intramolecular rearrangements comprising conversion of trigonal-bipyramidal to tetragonal-pyramidal geometry or *vice versa*.