CHEMISTRY OF CHLORITES

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A comprehensive review of the chemistry of chlorites is presented. The following are four of the most important items of the newer knowledge given:

The decomposition of chlorites in acid solution produces both chlorine dioxide and chlorates in a molar ratio usually greater than 2 to 1, respectively, which is nearly independent of the conditions. The rate of the decomposition is greatly influenced by conditions, especially pH.

The reaction between hypochlorite and chlorite also varies with pH. The primary reaction, at least under acid conditions, is the evolution of chlorine dioxide. Chlorates are formed by a slow reaction while the chlorine dioxide disappears.

Formaldehyde liberates chlorine dioxide from sodium chlorite even under conditions where the latter would otherwise be stable.

Both cellulosic and noncellulosic materials have been treated with chlorite. The resulting products have better qualities than were obtained with older treatments. Wood pulp, textiles, and sugar sirup are examples of products whose qualities may be improved by the use of chlorites.

UNTIL recently the important inorganic compounds of chlorine have been the chlorides, hypochlorites, and chlorates. Perchlorates may be classed as a comparatively recent development while chlorites are a chemical novelty now finding several commercially important applications. Because these compounds are so closely related, the neglect of the chemistry of the chlorites and, indeed, of any of the members of this series, impresses a handicap on the study of the chemistry of all the others.

The many apparently contradictory reports in the literature of the chlorites have not yet been resolved, as they have been in the case of the other oxy compounds of chlorine, by a great mass of experimental evidence. The use of the glass electrode for determining the pH of a solution of an oxidizing agent has only recently been applied to clarifying the properties of some of these compounds. With chlorites the pH values of the reacting solutions promise to be the basis upon which an orderly chemical understanding can be built.

This review cannot completely present the history of the chlorites nor all their technical details. In many cases only typical or most interesting data are reported. While only sodium chlorite is available commercially, various other chlorites which are desirable for experimental purposes may readily be prepared from common chemicals.

Formation and Production

The historical development of the chlorites, first prepared a century ago as the culmination of a series of discoveries, is discussed by Mellor (*32*) and Gmelin (*16*). It is apparent that, while the theories of that time were inadequate, the early workers were keen observers whose experimental records are still accurate.

Two molecules of hypochlorite may form one of chlorite and one of chloride. Thus, Gay-Lussac (*15*) observed the formation of chlorites in bleaching powder solutions exposed to sunlight, and Wolters (*56*), in attempting to establish the constitution of bleaching powder, found that *unterchlorige Säure* (Cl_2O) and bleaching powder slowly formed chlorous and chloric acids in dilute solution without heating.

The formation of chlorites in hypochlorites during storage became evident as a result of the study of analytical methods. In many investigations agreement between the analytical methods was found for freshly prepared solutions, but after storage, the oxidizing value shown by the titration of liberated iodine with thiosulfate was higher than by the best methods based on arsenious oxide. The data of Bhaduri (*3*) show a 2 per cent difference between these titrations after storage for a day in diffuse light or a month in the dark. Kolthoff (*23*) ascribed such differences to the formation of a chlorite.

Foerster and Dolch (*14*) found that the velocity of the reaction forming chlorites from hypochlorites was slow compared to the succeeding reaction by which chlorites and hypochlorites formed chlorates. The preparation of chlorites from hypochlorites thus requires that the second of these reactions must be avoided. Repeated references to the formation of chlorites when hypochlorites were exposed to light indicate that this might be a means of controlling the products. Jacquemain and Doll (*20*) found that the concentration of the chlorite passed through a maximum upon long continued exposure of a hypochlorite solution to diffuse light. This was in agreement with the results which we had previously secured by the use of various sources of artificial light. Only small concentrations of chlorite were obtained, as its production could not be sufficiently enhanced or its consumption to form chlorates inhibited in the illuminated solutions.

Since syntheses from hypochlorites fail to produce chlorites in usable quantities, chlorates appear as the next most logical source. Direct reduction of chlorates to chlorites has never been accomplished, chlorides being formed as the product of such attempts. The chlorates may, however, be reduced to chlorine dioxide as an intermediate product and then transformed into chlorites.

Chlorates were treated with acids by several early chemists who expected to obtain chlorine, but the gaseous products had varying properties. Davy (*10*) suggested that, while chlorine was produced if a manganese compound was present when hydrochloric acid reacted with a chlorate, "euchlorine" was formed in its absence. Hydrochloric acid could be replaced by a chloride and sulfuric acid with similar results. When sulfuric acid acted upon solid chlorate in the absence of a chloride, those properties were enhanced which distinguished "euchlorine" from chlorine. In modern terminology "euchlorine" would be a mixture of chlorine and chlorine

dioxide; and the gas obtained by the last mentioned method of preparation would be richer in chlorine dioxide.

Millon (*34*) described still another mixture of gases produced by the action of nitric acid on potassium chlorate. This reaction took place even in the presence of reducing agents, such as tartaric acid, which caused the simultaneous evolution of carbon dioxide. If potassium chlorate, arsenic trioxide, and nitric acid were used, the pure *acide chloreux* ClO_3 would be evolved. The modern formula for this gas would be Cl_2O_3. It is now generally believed that Millon's gas, as it was later called, was a mixture of chlorine dioxide and chlorine. Millon thought that using oxalic acid as the reducing agent, the gas produced was chlorine dioxide, and ascribed to it the same formula, ClO_4, as he did to the gas produced from potassium chlorate by the action of sulfuric acid.

The chemical pioneers thus laid the groundwork for most of the reactions which take place between a chlorate and an acid. The use of these reagents was long a favorite method for the preparation of chlorine:

$$KClO_3 + 6HCl = KCl + 3H_2O + 3Cl_2 \quad (1)$$

The same reagents may, under different conditions, yield both chlorine dioxide and chlorine:

$$2KClO_3 + 4HCl = 2ClO_2 + Cl_2 + 2KCl + 2H_2O \quad (2)$$

Just as the chlorine prepared by this method was frequently contaminated with chlorine dioxide, so more chlorine in proportion to chlorine dioxide is obtained than the theoretical quantity according to Equation 2.

When concentrated sulfuric acid reacts with a solid chlorate, an explosion of chlorine dioxide may result. Dilution of the acid with water or of the chlorate with an inert material (*2*) have been suggested as means of controlling this reaction. Ferran (*13*) stated, without specifying the products, that this reaction has been used commercially. The great disadvantage of this process is that only two thirds of the chlorine can be converted to chlorine dioxide, one third forming perchlorate:

$$3KClO_3 + 3H_2SO_4 = 2ClO_2 + HClO_4 + H_2O + 3KHSO_4 \quad (3)$$

Laboratory Methods for Chlorites

Calvert and Davies (*6*), using a slurry of potassium chlorate and oxalic acid, found the yield of chlorine dioxide dependent upon the proportions of the two reagents, but never obtained a theoretical yield based on the equation:

$$2KClO_3 + 2(COOH)_2 = 2ClO_2 + 2CO_2 + (COOK)_2 + 2H_2O \quad (4)$$

This process, known by the names of various workers who introduced modifications, has become the common laboratory method for the production of chlorine dioxide since the carbon dioxide formed renders the chlorine dioxide less likely to explode.

In this reaction the oxalic acid serves both as an acid to produce a salt and as a reducing agent. In practice, several times the theoretical amount of oxalic acid is required in order to obtain even a 50 per cent yield of chlorine dioxide based on the chlorate taken. Schacherl (*39*) suggested the addition of sulfuric acid to the mixture of Calvert and Davies. While this appears to be a logical development in accordance with Equation 5, it has not been generally adopted:

$$2KClO_3 + (COOH)_2 + 2H_2SO_4 = 2ClO_2 + 2CO_2 + 2H_2O + 2KHSO_4 \quad (5)$$

The subsequent conversion of chlorine dioxide into a chlorite may be accomplished in various ways. Millon (*34*) has been credited with first producing chlorites by the action of chlorine dioxide on an alkali, but Martens (*31*) previously accomplished this transformation with at least a partial understanding of the result. This is not an efficient means of producing chlorite since half of the chlorine dioxide is lost by the formation of chlorate:

$$2ClO_2 + 2NaOH = NaClO_2 + NaClO_3 + H_2O \quad (6)$$

Reychler (*38*) suggested the use of the solution of a peroxide as reducing agent to yield all of the chlorine dioxide as chlorite:

$$2ClO_2 + Na_2O_2 = 2NaClO_2 + O_2 \quad (7)$$

Calcium peroxide is preferable and can be conveniently prepared by mixing 100-volume hydrogen peroxide with a well-cooled solution of milk of lime. When absorption is complete, the mixture need only be filtered to obtain a usable solution of calcium chlorite. Of the other peroxides that might be used, barium is probably the most important since an insoluble barium salt may be subsequently precipitated to obtain a solution of chlorous acid.

Other reducing agents may be used in alkaline solution for the absorption and reduction of chlorine dioxide so that a quantity of chlorite substantially equivalent to the chlorine dioxide will result. Carbon, sulfur, sugar, and paper pulp are suitable for this use (*47*), but the reduction must take place before the gas reacts with the alkali since chlorates are not reduced under these conditions.

When chlorine dioxide is accompanied by chlorine in the evolved gases, direct absorption is not practical. With alkali alone, the hypochlorite formed from the chlorine might react with the chlorite when the solution was further processed. The use of reducing agents—for example, hydrogen peroxide—to remove chlorine would require uneconomical quantities. It is therefore desirable to remove the chlorine from the chlorine dioxide before absorption. The earliest suggestion was fractional condensation of the chlorine dioxide to a liquid. While liquid chlorine dioxide can be relatively safely handled on a small scale, it is very dangerous if collected in quantity.

Fractional crystallization of the chlorate and chlorite produced by absorption in alkali is difficult because both salts are about equally soluble. By proper adjustment of the concentrations of salts, it is possible to cause calcium chlorite to precipitate when the chlorine dioxide reacts with an aqueous suspension of lime (*28, 45*). The chlorine dioxide can be selectively absorbed in salt solutions or sulfuric acid and then subsequently removed by aeration (*48*). Separation can also be accomplished by utilizing the differences in rates of reaction of chlorine and chlorine dioxide with alkalies (*46, 54*). This process is suitable for laboratory use since, by passing the gases through a moderately strong solution of sodium hydroxide, such as 6–10 per cent, all of the chlorine and some of the chlorine dioxide will react with the alkali. Most of the chlorine dioxide will be carried along with the exit gases and can then be absorbed in a peroxide solution. Sufficient inert gas should be present in the gas mixture to keep the partial pressure of chlorine dioxide below the explosive limits (*42*).

Existence and Physical Properties

Millon (*34*) prepared the chlorites of potassium, sodium, barium, strontium, lead, and silver. The last two he found to be only slightly soluble. He made attempts to analyze these compounds and to establish that their composition was different from that of salts of previously known oxychlorine acids. In comparatively recent times Bruni and Levi (*5*) began a study of chlorites which, in the hands of Levi and his

co-workers, has developed into an extensive and sustained investigation. In addition to the simple chlorites of many metals, they have prepared numerous complex chlorites. The results of this work up to 1927 were compiled by Gmelin (*16*) and subsequently by Levi (*25*).

Both sodium and calcium chlorites are very stable in solid form and in slightly alkaline solutions. They can be stored for extended periods with only slight decomposition. Numerical data on the stability of sodium chlorite have been presented in a previous communication from this laboratory (*42*).

Levi (*24*) found the decomposition temperature of sodium chlorite to be 180–200° C. We have determined the decomposition temperature, defined as the temperature at which a white smoke is evolved with a popping sound, by dropping sodium chlorite on a heated Dennis copper bar. This temperature varies with the moisture content from 202° C. with 3.7 per cent of water to 177° C. with 10.7 per cent. The fusion temperature, obtained by spreading a train of the salt on the cold copper bar and then heating to actual fusion, falls irregularly in the range of 250° to 257° C. as the composition of the solid varies.

Chlorite solutions indicate by their chemical behavior that chlorous acid must be fairly strong. Addition of hydrochloric acid to solutions of sodium chlorite yields approximately the same pH as if pure water had been used in place of the chlorite solution. Davidson (*9*) employed a similar titration method to determine the ionization constant of hypochlorous acid. The ionization constant, 1.10×10^{-2}, determined by Barnett (*1*) shows that chlorous acid has about the same strength as oxalic and dichloroacetic acids.

Smith, Pitzer, and Latimer (*40*) recently determined the entropy and heat of solution of silver chlorite.

A close similarity between the formulas of chlorites, chlorates, and hypochlorites suggests that the same precautions which are taken in handling the two better known salts should also be observed in handling chlorites. In laboratory experiments with chlorites, the greatest hazard is probably the easy production of chlorine dioxide, the gas which makes the utilization of chlorate and acid so dangerous. However, when this gas is diluted with a considerable volume of air, it is safe to handle. The conditions for the production of chlorine dioxide from chlorites can be better controlled than from chlorates, as will be discussed below.

Analysis

The study of the chemistry of chlorites involves the analytical determination of many compounds which are closely related chemically. These analyses usually depend upon causing particular components to react or not according to carefully controlled conditions. In any complete analysis the well-known error of determining the difference between two large numbers occurs repeatedly, and there are also the uncertainties of the exact reactions of certain compounds. The data have, therefore, been rounded off to fewer significant figures than is customary with the same analytical titrations.

The details of the methods are not necessary here, but Table I shows the reagents and reactants used in the analysis of solutions. The analytical reagents for each determination are given in the first column. "(NaOH)" indicates that strong sodium hydroxide may be necessary to prevent further changes in the sample—e. g., the loss of gases. The reacting compounds and their oxidation equivalents, shown in the second column, provide the bases for calculating the results. These particular methods were selected because they were applicable to a wide range of analytical problems. It soon became evident that special care was necessary if the results were to be suitable for any but the most approximate determinations.

Table I. Analysis of Chlorite Solutions

Reagents	Reactants in Equivalents
(NaOH) NaBr + strong HCl + KI + $Na_2S_2O_3$	6[ClO_3^-], 5[ClO_2], 4[ClO_2^-], 2[ClO^-], 2[Cl_2]
KI + acid + $Na_2S_2O_3$	5[ClO_2], 4[ClO_2^-], 2[ClO^-], 2[Cl_2]
Strong NaOH + KI + acid + $Na_2S_2O_3$	2[ClO_2], 4[ClO_2^-], 2[ClO^-], 2[Cl_2]
(NaOH) As_2O_3 + $NaHCO_3$ + I_2	2[ClO^-], 2[Cl_2]
(NaOH) HNO_3 + $AgNO_3$ with K_2CrO_4 as indicator	[ClO^-], 2[Cl_2], [Cl^-]
Standard HCl + $Na_2S_2O_3$ + standard NaOH	[H^+] or [OH^-]

The addition of potassium iodide to strong hydrochloric acid in the determination of the total oxidizing value of all the compounds (the first method in Table I) would be expected to liberate an excess of iodine because of the oxidation of hydriodic acid by the air. When the analysis is properly conducted, there are no indications of such an excessive liberation of iodine. Instead there appears to be a tendency for the results to be low. To keep this error at a minimum, it has been found necessary to check all carboys of hydrochloric acid, for occasionally one has been found to give several per cent low for the chlorate content of C. P. potassium chlorate. The ferrous sulfate–potassium permanganate method, frequently used for the determination of chlorates, yielded erratic results when all possible oxidizing agents were present.

The addition of sodium hydroxide, required when chlorine dioxide is present, will cause hypochlorites to react with some reducing agents if they are also contained in the solution. Chlorides are a common impurity in the sodium hydroxide. Phosphates and other buffers add to the magnitude of the correction to be applied in the determination of the chlorides. Since the reaction between chlorine dioxide and sodium hydroxide is slow, it may be incomplete when the sample is titrated. Heat speeds this reaction but is not advisable in the presence of hypochlorite. Jeanes and Isbell (*21*) removed the gaseous products before analysis, but in some solutions there may be further reaction during the process of removal.

Various schemes have been suggested for the determination of chlorine in simple admixture with hypochlorites, but the methods are uncertain and unsatisfactory. No accurate method is available for the separate determination of these substances.

In the analysis of gases containing chlorine dioxide, the gas stream may be successively passed into a solution of sodium hydroxide and a suspension of calcium peroxide, or into a solution of potassium iodide. The analytical methods are the same as those used for the solutions. The compounds involved are as follows:

Absorb in NaOH and CaO_2; analyze as for solutions:

$$ClO^- = Cl_2$$
$$ClO_3^- + ClO_2^- = ClO_2 \text{ (sum of both absorbers)}$$

or $2ClO_3^- = ClO_2$ (in NaOH only)

$$\frac{ClO_2^- - ClO_3^-}{2} = Cl_2O_3 \text{ (in NaOH only)}$$

Absorb in neutral KI:

$$Na_2S_2O_3 \text{ (in neutral solution)} = ClO_2 + 2Cl_2$$
$$Na_2S_2O_3 \text{ (in acid solution)} = 5ClO_2 + 2Cl_2$$

or using standard HCl + $Na_2S_2O_3$ + standard NaOH:

$$Na_2S_2O_3 = 5ClO_2 + 2Cl_2$$
$$Na_2S_2O_3 + NaOH - HCl = ClO_2 + 2Cl_2$$

It rarely happens that the analytical titrations will give the exact balance of salts which would be expected from the equations for the absorption of chlorine and chlorine dioxide.

If the concentration of chloride exceeds that of hypochlorite in the sodium hydroxide solution, it may indicate either a further reaction in the absorber or the presence of hydrogen chloride in the original gaseous mixture. In one series of experiments the chlorite concentration in the sodium hydroxide solution exceeded the chlorate so persistently that chlorine trioxide might have been present. However, existence of this gas has been denied for many years on the basis of studies of absorption spectra. Recently Kantzer (*22*) claimed to have produced chlorine trioxide and differentiated its absorption spectrum from that of chlorine dioxide. Goodeve and Richardson (*17*) repeated these experiments without finding chlorine trioxide. It might afford an explanation of some peculiar reactions of the chlorites, but as it has never been found in quantities much in excess of the analytical uncertainties, chlorine trioxide will be ignored in the subsequent discussion.

The calcium peroxide used for the absorption of chlorine dioxide is so insoluble that filtration leaves a scarcely detectable quantity of peroxide in solution. A thick cake of it is difficult to wash because of the ease with which it channels.

The analyses based on the use of only potassium iodide solution for absorbing the evolved gases require less time but are subject to some inaccuracies. Thus all acid-generating gases would be calculated as chlorine. Too high results for chlorine dioxide may be caused by excessive alkalinity of the potassium iodide solution.

Better analytical methods are highly desirable and, except for a few cases in which the components are limited in number, must be found in order to secure sufficient precision for detailed study of the mechanism of the reactions of chlorites.

Reactions of Chlorites

Many of the experiments on the reactions of chlorites alone in solution or in the presence of other substances were undertaken in an effort to gain a better understanding of bleaching processes, since both chlorine dioxide and chlorate have been observed during bleaching. It is difficult to conceive of any mechanism by which oxidizing values transformed into chlorate could be of any further service in bleaching. Therefore, economy demands that its formation should be kept at a minimum. Chlorine dioxide is a bleaching agent. The question thus arises as to whether its formation should be promoted for best bleaching. A definite answer has not been found; possibly it will depend upon the material being bleached.

Before these problems of bleaching can be solved, the reactions of chlorites must be reinvestigated in view of the confusion in the literature. Recent experimentation has demonstrated that pH is of great importance and that the conflicting observations can be clarified upon this basis. The subject leads into so many diverse phases that numerous further contributions are essential to a more complete knowledge of these reactions.

Decomposition

Almost all possible products which may exist in the solution have been supposed to affect the course of the decomposition of chlorites in acid solutions. Barnett (*1*) found that chlorides accelerated the decomposition of chlorites. Since chlorides are invariably present either as an impurity or as products of the decomposition, the chlorites cannot be commercially utilized in the absence of chlorides. When using commercial sodium chlorite, chloride and chlorate are always present but in varying amounts, depending upon the quality of material. As shown in Table II, an increase in chloride content does not further accelerate the reaction.

Table II. Effect of Salts on Chlorite Decomposition at 60° C.

Expt. No.	35	37	38	60	66	73	67
$NaClO_2$, mole/l.	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Additions per liter							
$NaClO_3$	...	...	10 g.	...	0.25 mole	...	0.25 mole
NaCl	...	5 g.	...	...	.....	...	.....
Time, hr.	1	1	1	0.5	0.5	0.5	0.5
pH	4	4	4	3.8	4.0	2	1.7
Buffer	NaOAc	NaOAc	NaOAc	PO_4	PO_4	HOAc	PO_4
$NaClO_2$ decomposed, mole/l.	0.102	0.086	0.090	0.041	0.037	0.247	0.254
Products formed, mole/l.							
ClO_2	0.050	0.044	0.044	0.019	0.017	0.121	0.117
$NaClO_3$	0.022	0.016	...	0.008	.....	0.053	.....
NaCl	0.028	...	0.026	0.022	0.011	0.066	0.06+
Total	0.100	...	...	0.049	.....	0.240	.....
$ClO_2/NaClO_3$	2.3	2.8	...	2.4	.....	2.3	.....

Various workers have speculated concerning the possibility that chlorous and chloric acids can form chlorine dioxide by a reversal of hydrolysis:

$$HClO_2 + HClO_3 = 2ClO_2 + H_2O \quad (8)$$

But this idea seems to have originated with Oechsli (*35*) without any experimental verification. Table II shows that when a chlorate was added to the chlorite in acid solution, there was no evidence of enhanced production of chlorine dioxide, as would be expected if this or any other mechanism involving chlorates was contributing to its formation.

Table III compares the results obtained when air is passed continuously through the reacting solution with those when the chlorine dioxide is not so removed. In our earliest experiments the methods for determining chlorine dioxide in the reacting solution had not been developed, so the gas was removed by a final short aeration. Since the total decomposition of the chlorite is not dependent upon aeration, this reaction is not reversible. The early experiments may indicate that less chlorine dioxide and more chlorate resulted when the chlorine dioxide remained in the solution. While this suggests that chlorate is formed from chlorine dioxide, we do not regard this evidence as conclusive.

The data in a previous communication from this laboratory (*42*) indicate that the proportions of the products are the same at room temperature as at 60° C. Both temperatures are therefore included in Table IV, which shows the effect of concentration upon the decomposition of sodium chlorite at pH 4. The concentrated solutions evolved so much chlorine dioxide that elevated temperatures were not advisable, while

Table III. Effect of Chlorine Dioxide Removal on Chlorite Decomposition

Expt. No.	22	6	23	9	60	68
$NaClO_2$, mole/l.	0.25	0.25	0.25	0.25	0.25	0.25
Air stream, hours						
Above soln.	5.5	0	5.5	0	0.5	0
Through soln.	0.5	6.0	0.5	6.0	0	0.5
Temp., ° C.	Room	Room	62	62	60	60
pH	2.5	2.5	4	4	3.8	3.8
Buffer	HOAc	HOAc	NaH_2PO_4	NaH_2PO_4	NaH_2PO_4	NaH_2PO_4
$NaClO_2$ decomposed, mole/l.	0.108	0.108	0.105	0.097	0.041	0.039
Products formed, mole/l.						
ClO_2	0.033	0.053	0.027	0.048	0.019	0.020
$NaClO_3$	0.026	0.026	0.039	0.023	0.008	0.010
NaCl	0.017	0.028	0.030	0.027	0.022	0.013
Total	0.076	0.107	0.096	0.098	0.049	0.043
$ClO_2/NaClO_3$	1.3	2.0	0.7	2.1	2.4	2.0

TABLE IV. EFFECT OF CONCENTRATION ON CHLORITE DECOMPOSITION

Expt. No.	15	82	83	74	77	75	60[a]	58	52	76	79
$NaClO_2$, moles/l.	2.4	2.6	2.6	2.6	1.25	1.25	0.25	0.25	0.25	0.005	0.005
Time, hr.	6	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1/2	1/2	6
pH	4[b]	4[b]	4[b]	4[b]	4[b]	4[b]	3.7–3.9	3.8–4.0	4[b]	4.0	3.9
Buffer	NaH_2PO_4	NaH_2PO_4	NaOAc	NaOAc	NaH_2PO_4	NaOAc	PO_4	PO_4	NaOAc	NaOAc	NaOAc
Temp., ° C.	25	Room	Room	Room	Room	Room	60	60	60	60	60
Air stream	Through	Above	Through	Above	Above	Above	Above	Above	Above	Above	Above
$NaClO_2$ decomposed, mole/l.	0.207	0.114	0.118	0.127	0.263	0.147	0.041	0.024	0.038	0.0006	0.0009
Products formed, mole/l.											
ClO_2	0.089	0.052	0.057	0.066	0.062	0.071	0.019	0.010	0.016	0.0003	0.0007
$NaClO_3$	0.048	0.024	0.040	0.038	0.097	0.034	0.008	0.004	0.007	0.0003	0.0003
NaCl	0.041	0.075	0.051	0.042	0.095	0.042	0.022	0.011	0.013	0.0006	0.0008
Total	0.178	0.151	0.148	0.146	0.254	0.147	0.049	0.025	0.036	0.0012	0.0018
$ClO_2/NaClO_3$	1.9	2.2	1.4	1.7	0.6	2.1	2.4	2.5	2.3	..	2.3

[a] PO_4 more concentrated than in experiment 58.
[b] Estimated from the buffer used.

TABLE V. EFFECT OF pH ON CHLORITE DECOMPOSITION AT 60° C. AFTER 30 MINUTES

Expt. No.	63	64	65	73	55	59	56	71	72	60a	58	52	53	54	61	81
$NaClO_2$, mole/l.	0.25	0.05	0.05	0.25	0.20	0.25	0.20	0.25	0.25	0.25	0.25	0.25	0.20	0.20	0.25	0.25
pH	0.6	0.5	1.3	2.0	2.0	2.1–2.3	2.8	3.2	3.2	3.7–3.9	3.8–4.0	4	4.6	5.3	5.9	7.0
Buffer	$NaHSO_4$	$NaHSO_4$	H_3PO_4	HOAc	HOAc	PO_4	HOAc	HOAc	HOAc	PO_4	PO_4	NaOAc	NaOAc	NaOAc	PO_4	PO_4
$NaClO_2$ decomposed, mole/l.	0.254	0.051	0.048	0.247	0.189	0.232	0.165	0.165	0.156	0.041	0.024	0.038	0.0059	0.0017	0.0014	0.015[b]
Products formed, mole/l.																
ClO_2	0.123	0.024	0.022	0.121	0.079	0.104	0.062	0.072	0.075	0.019	0.010	0.016	0.0030	0.0006	0.0009	0.001[b]
$NaClO_3$	0.051	0.010	0.010	0.053	0.029	0.049	0.035	0.035	0.031	0.008	0.004	0.007	0.0014	0.0011	0.0004	0.008[b]
NaCl	0.068	0.015	0.018	0.066	0.060	0.060	0.046	0.047	0.043	0.022	0.011	0.013	0.0006	0.0008	0.0027	0.010[b]
Total	0.242	0.049	0.050	0.240	0.168	0.213	0.143	0.154	0.149	0.049	0.025	0.036	0.0050	0.0025	0.0040	0.019[b]
$ClO_2/NaClO_3$	2.4	2.4	2.2	2.3	2.7	2.1	1.8	2.1	2.4	2.4	2.5	2.3	2.1	0.5	2.3	0.1

[a] PO_4 more concentrated than in experiment 58.
[b] After 5 hours.

at room temperature the changes in dilute solutions were too small to be accurately determined. The ratio of chlorine dioxide to chlorate approximates 2 in many experiments at the higher concentrations. With sodium chlorite concentrations of 0.25 *M* or less, the ratio of these products was definitely greater than 2, which may indicate that chlorine dioxide and chlorate are the result of separate reactions. Aeration or the nature of the buffers used was not consistent in effect.

To show the effect of pH, experiments were selected in which 100 ml. of sodium chlorite solution in various concentrations were allowed to react for 30 minutes. Any evolved gases were carried to an absorber by an air stream above the surface of the reacting solution. Table V shows that below pH 4.6 the ratio of chlorine dioxide formed to chlorate formed was consistently greater than 2, with the exception of experiment 56. The buffering chemical or the exact concentration of sodium chlorite did not affect this ratio. At higher pH values the extent of the reaction was so small that accuracy was low. At pH 7 there may be a tendency toward the production of chlorate without the formation of chlorine dioxide.

The data for the production of chlorine dioxide and chlorate at 60° C. from 0.25 *M* sodium chlorite solutions are plotted in Figure 1. The extent of their formation increases greatly as the pH is lowered from 4 to 2. According to the ionization constant of chlorous acid at lower temperature, as determined by Barnett (*1*), the ratio between chlorous acid and chlorite ion should change greatly in this same range of pH. Below pH 2 exhaustion of the chlorite masks any possible effect of pH.

The equation which has been written for the decomposition of chlorous acid shows both chlorine dioxide and chlorate as products in a ratio of 2 to 1:

$$4HClO_2 = 2ClO_2 + HClO_3 + HCl + H_2O \qquad (9)$$

The chlorine in two of the products is in a higher state of oxidation than in chlorous acid. Since the experimentally determined ratio for these products is frequently greater than 2, it is possible that Equation 9 is the summation of equations representing two or more reactions.

The formation of chlorate has been observed without any accompanying chlorine dioxide when solid sodium chlorite is heated (*24*, *42*):

$$3NaClO_2 = 2NaClO_3 + NaCl \qquad (10)$$

Chlorates are also formed in the slow decomposition of alkaline solutions of chlorites. The data for pH 7 in Table V may indicate that there is a gradual transition from this reaction under alkaline conditions to the type of decomposition found in acid solution. If the same mechanism is assumed to be involved in chlorate formation in acid solution, subtraction of Equation 10 (converted to acid equivalents) from two times Equation 9 will give the following equation for the production of chlorine dioxide:

$$5HClO_2 = 4ClO_2 + HCl + 2H_2O \qquad (11)$$

The experiments in buffered solutions have not yielded clear evidence of such a reaction. In some of his experiments Barnett (*1*) produced chlorine dioxide equal to four fifths of the consumption of chlorite by boiling solutions containing purified sodium chlorite and perchloric acid. We were unable to obtain these results on repeating his experiments with commercial sodium chlorite, perhaps because of the difference in the purity of the chlorites.

In some unreported experiments the rate of evolution of chlorine dioxide at pH 4 was nearly proportional to the square of the chlorite concentration, although the factor varied greatly with the particular buffer salt employed. The red color of concentrated solutions may be an indication of a molecular complex including chlorine dioxide, which could be an intermediate step in the decomposition of the chlorite. The mechanism of the reaction which forms chlorine dioxide is still obscure. Chlorides and chlorates may have a small effect on the decomposition of a chlorite solution while hy-

drogen ion affects only the rate. Thus, the decomposition is inherent in the chlorite itself. Speculations on the mechanism of this reaction must also include the approximate constancy of the proportions of the products when the conditions of the experiments were quite diverse.

Effect of Chlorine and Hypochlorites

The introduction of chlorine or hypochlorites into the solution of a chlorite considerably modifies the course of the reactions. Foerster and Dolch (*14*) showed that in alkaline solution the formation of chlorites was one step of the well-known transformation of hypochlorites into chlorates. The formation of chlorites is a slow reaction which limits the rate of chlorate formation. Since for rapid formation of chlorate it is necessary to overchlorinate the alkali, the equation is frequently written to indicate that hypochlorous acid and hypochlorite ion participate in the reaction:

$$HClO + 2ClO^- = H^+ + ClO_3^- + 2Cl^- \quad (12)$$

The intermediate formation of chlorites may be represented by such equations as:

$$2NaClO = NaClO_2 + NaCl \quad (13)$$

$$NaClO_2 + NaClO = NaClO_3 + NaCl \quad (14)$$

Chlorine dioxide has also been observed as a product of the reaction of hypochlorites upon chlorites. Foerster and Dolch (*14*) believed that chlorate was the primary product and that chlorine dioxide was formed by the reaction of chlorous and chloric acids. It was pointed out above in the discussion of the decomposition of chlorites that this does not appear probable. Under slightly different conditions the same authors found that chlorine dioxide and a hypochlorite would react to form a chlorate:

$$2ClO_2 + NaClO + 2NaOH = NaCl + 2NaClO_3 + H_2O \quad (15)$$

Cunningham and Losch (*8*) and Levi and Tabet (*27*) independently discovered that the addition of chlorine to a chlorite solution would liberate chlorine dioxide. Logan (*30*) found that these solutions could be used in bleaching while Parsons and Jackson (*37*) suggested the substitution of hypochlorite for chlorine. Such bleaching frequently resulted in the formation of some chlorine dioxide and chlorate. Studies of the effect of varying conditions show that among other factors, pH is important in determining not only the proportions of the products but also the course of the reaction between chlorite and hypochlorite.

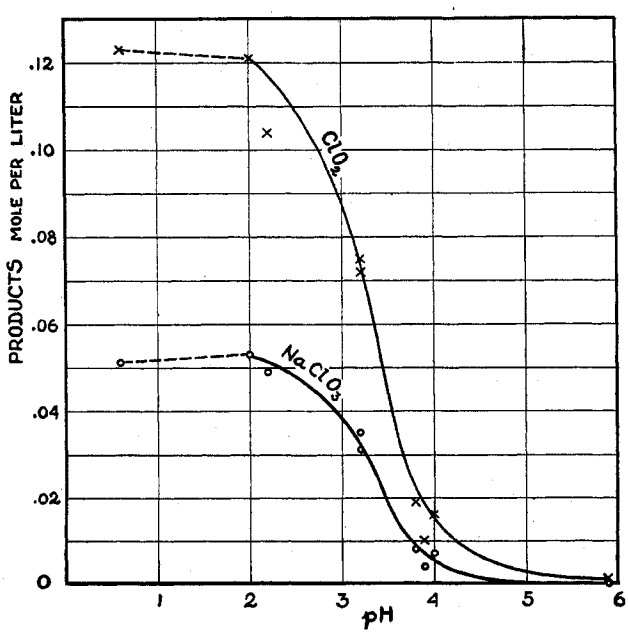

FIGURE 1. PRODUCTION OF CHLORINE DIOXIDE AND CHLORATE AT 60° C. FROM SODIUM CHLORITE SOLUTIONS

The cornerstone of our whole understanding of the reaction between a hypochlorite and a chlorite is the observation that chlorine dioxide is a primary product of the reaction. There is no definite relation between the proportions of chlorine dioxide and chlorate formed. Under certain conditions solutions analyzed as soon as the reagents were mixed contained more chlorine dioxide than solutions of the same composition which had stood 30 minutes. Table VI shows the data for analyses made immediately after mixing and again on the same solution after 30 minutes. The evolved gases were less than 1 per cent of the total moles so that they were neglected in these computations. In the experiments of Table VI and all others to be mentioned here, the chlorite was placed in a buffer solution and the hypochlorite solution added to the mixture at room temperature. Both chlorine dioxide and chlorate were formed as soon as the solutions were mixed, but on standing the chlorine dioxide and hypochlorite disappeared in amounts which agree quite well with the equation,

$$2ClO_2 + HClO + H_2O = 2HClO_3 + HCl \quad (16)$$

which is essentially the same as Equation 15.

The reaction of chlorine with a chlorite is nearly quantitative according to the equation:

$$2NaClO_2 + Cl_2 = 2ClO_2 + 2NaCl \quad (17)$$

Making allowance for the hydrolysis of chlorine, the same action for hypochlorous acid would be

$$2HClO_2 + HClO = 2ClO_2 + HCl + H_2O \quad (18)$$

but the data are not sufficient to decide whether this actually represents the reaction. Addition of Equations 16 and 18 gives the simplest equation for the formation of chlorate. Various other suggested mechanisms for the reaction of chlorine dioxide to form chlorate end in the same summation. The analytical methods give no indication of the intermediate reactions so that the actual mechanism of chlorate formation is not evident.

TABLE VI. EFFECT OF TIME ON CHLORITE-HYPOCHLORITE REACTION AT pH 5.8–5.7 AND ROOM TEMPERATURE

	Mole per 400 Ml.					
Expt. 54	Added	0 time	Immediate change	30 min.	Slow change	Theory
$NaClO_3$	0.0003	0.0023	+0.0020	0.0042	+0.0019	+0.0019
ClO_2	....	0.0028	+0.0028	0.0009	−0.0019	−0.0019
$NaClO_2$	0.0051	0	−0.0051	0	0	.....
NaClO	0.0103	0.0066	−0.0037	0.0060	−0.0006	−0.00095
NaCl	0.0028	0.0070	+0.0042	0.0078	+0.0008	+0.00095
Total	0.0185	0.0187	.....	0.0189	.....	.....

Two molecules of chlorite react with one of hypochlorite to form chlorine dioxide as in Equation 18, while Equation 14 shows that one molecule of each is required for the formation of chlorates. Residual hypochlorite remaining after the formation of chlorine dioxide should permit the slow formation of chlorate to continue and thereby produce more than if the amount of hypochlorite were restricted. Table VII shows experiments in which three different proportions of chlorite

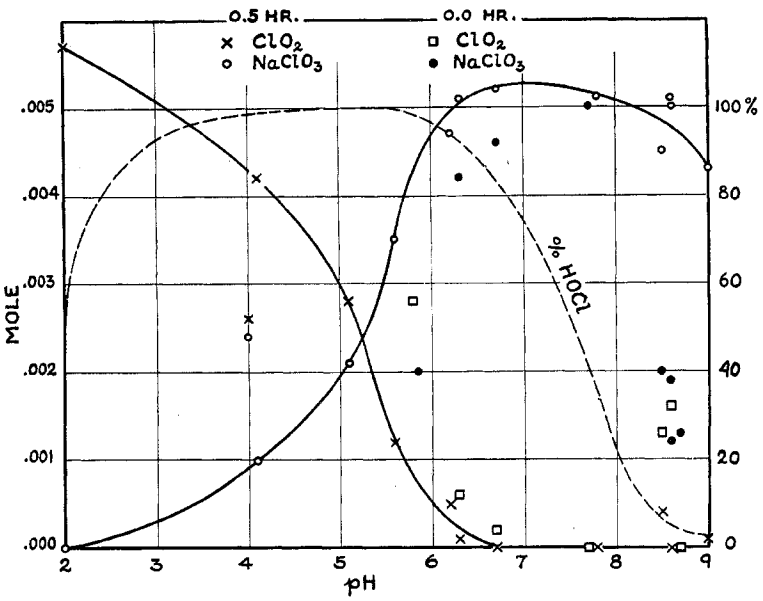

FIGURE 2. EFFECT OF pH ON CHLORINE DIOXIDE AND CHLORIDE FORMATION FROM CHLORITE-HYPOCHLORITE REACTION

to hypochlorite were allowed to react. When the molecular ratio was 2 to 1, chlorine dioxide formation predominated and persisted for 30 minutes as the hypochlorite was exhausted in the immediate reaction. At ratios of chlorite to hypochlorite of 1 to 2 and 1 to 4, the immediate chlorate formation was increased while that of the chlorine dioxide was decreased. This tendency continued during the 30-minute reaction time so that with the greatest quantity of hypochlorite, chlorine dioxide was completely changed into chlorate.

TABLE VII. EFFECT OF PROPORTIONS OF CHLORITE AND HYPOCHLORITE ON THE REACTION AT ROOM TEMPERATURE

(0.005 mole $NaClO_2$; soduim acetate buffer)

	0 Time			30 Minutes		
Expt. No.	69	54A	106	100	40	107
$NaClO_2$:NaClO, mol.	2:1	1:2	1:4	2:1	1:2	1:4
pH	5.5	5.8	5.7	5.5	5.6	5.7
Mole per 400 ml.						
$NaClO_2$ loss	0.0047	0.0051	0.0051	0.0046	0.0051	0.0051
NaClO loss	0.0025	0.0037	0.0047	0.0025	0.0045	0.0052
Total loss	0.0072	0.0088	0.0098	0.0071	0.0096	0.0103
ClO_2 gain	0.0037	0.0028	0.0023	0.0035	0.0012	0.0001
$NaClO_3$ gain	0.0003	0.0020	0.0028	0.0005	0.0035	0.0050
NaCl gain	0.0033	0.0042	0.0047	0.0031	0.0042	0.0061
Total gain	0.0073	0.0090	0.0098	0.0071	0.0089	0.0112

Higher temperature and concentration appear to favor the reaction between chlorine dioxide and any excess hypochlorite, with a resultant increase in the rate of chlorate formation by the slower reaction. The effect of these factors upon the instantaneous reaction cannot be determined. Multiple repetitions of the comparison indicate that chlorine probably has the same effect as hypochlorite at the same pH values.

Figure 2 shows how the formation of chlorine dioxide and chlorate depends upon the pH of the solution, immediately on mixing and after 30 minutes. Secondary reactions may have occurred since the solutions were not aerated. In these experiments 0.005 mole of sodium chlorite and 0.010 of sodium hypochlorite were mixed in 400 ml. of solution so that there was always an excess of hypochlorite. At pH 2 and 4 chlorine dioxide was liberated without any tendency to chlorate formation. A second experiment at pH 4 indicated nearly equal formation of these two products. Phosphate buffers were substituted for the acetate buffers previously used. Because the second hydrogen of phosphoric acid and hypochlorous acid have ionization constants of nearly the same magnitude, the relations of incomplete neutralization of weak acids, rather than pH alone, will govern the equilibria between the ionic and molecular forms resulting from the hypochlorite. Underwood and Mack (*44*) suggested that the salt effect of uni-bivalent buffers and of uni-univalent buffers may account for differences in the results of bleaching with hypochlorite. The logic of both suggestions is similar.

As the pH of the solution is increased, the rates of the reactions are altered until chlorate is the sole product. The analyses shown as individual points in Figure 2 indicate higher ratios of chlorine dioxide to chlorate immediately on mixing than after standing. These observations are in agreement with the concept of a slow reaction for the formation of chlorates.

Above pH 8 there is a region in which the results are inconclusive. Using bicarbonate to adjust the pH, the equilibria again involved two weak acids of nearly the same ionization constants. In some of the experiments there was evidence of chlorine dioxide formation, and in experiments more closely related to bleaching, chlorine dioxide has been observed so frequently as to make its formation appear to be the normal reaction. By titrating the solutions with acid, it appears that mixtures of the sodium salts or mixtures of the calcium salts begin to evolve chlorine dioxide at about pH 8.6. In these weakly alkaline solutions chlorine dioxide may be formed and then be consumed in the formation of chlorates. It is possible that chlorates are also formed as the primary product of other reaction mechanisms.

Figure 2 also includes a curve showing the per cent hydrolysis of sodium hypochlorite at different pH values. These data are taken from the tabulations of Elöd and Vogel (*12*) and Opfermann and Hochberger (*36*). At low values of pH where chlorine dioxide is stable, free chlorine and hypochlorous acid are both present. From pH 4 to 6, where hypochlorous acid is the predominant form, the products change their proportions. As hypochlorite ion becomes appreciable, chlorate formation increases until the pH is so high that the solutions become relatively stable. This suggests that the hydrolysis of chlorine and hypochlorite may determine the nature of the products formed by the reactions between chlorites and hypochlorites.

Chapin (*7*) found in his study of the conversion of hypochlorite into chlorate that it was complete between pH about 5 to 8. He heated 0.02 *M* sodium hypochlorite at 80° C. for 9 days without effecting complete reaction outside these limits. Either our introduction of ready-formed chlorite greatly increased the velocity of the reaction or there are controlling equilibria which hinder the completion of the reaction.

In more alkaline solutions the mixtures of hypochlorite and chlorite, just as hypochlorite alone, are more stable. In our experiments the mixtures did not change significantly during 30 minutes at pH 11, but the exact value of pH at which such stability is first observed probably varies with other condi-

tions. By using different experimental methods and increasing the temperature to 50° C., the rate of the reaction in alkaline solution was determined. Velocity constant K showed the least variation when calculated on the basis of an equation of the second order. Table VIII shows the effect upon the values for K_2 of varying concentrations of chlorite and hypochlorite, which were always initially equimolar, and of sodium hydroxide. These experiments were calculated for a specific purpose so that the values of K_2 are based upon the percentage of original oxidizing power with minutes as the unit of time. Several analyses showed that the consumption of hypochlorite and chlorite involved equal numbers of molecules of each. Equation 14 represents such a reaction of the second order. The variation of the numerical values indicates that this is not the complete formulation of the mechanism of this reaction. Using a more limited range of conditions, Foerster and Dolch (*14*) found a similar variation in the values of K_2. The order of magnitude of their values for K_2 agree at similar concentrations with those shown in Table VIII after correction for the difference in units.

TABLE VIII. K_2 VALUES FOR RATE OF CHLORATE FORMATION IN SODIUM HYDROXIDE AT 50° C.

Equal Concn. of $NaClO_2$ and NaClO	NaOH Concentration			
	4.0 *M*	1.5 *M*	0.5 *M*	0.08 *M*
1.755 *M*	2×10^{-4}	8.5×10^{-5}	5.3×10^{-5}	9×10^{-5}
0.75 *M*	4.5×10^{-5}	1.5×10^{-5}	1.0×10^{-5}	1.1×10^{-5}
0.25 *M*	1.0×10^{-5}	3×10^{-6}	2×10^{-6}	2.1×10^{-6}

The production of chlorine dioxide and chlorates from chlorites by the action of hypochlorites is accomplished by oxidation. Other oxidizing agents, such as sodium dichromate, sodium persulfate, lead dioxide, ozone, and bromine, will react in this same manner with a chlorite. Levi and his coworkers (*24*, *26*, *27*) made similar observations. Whether chlorine dioxide and chlorate are produced singly or together probably depends upon the conditions more than upon the specific oxidizing agent used with the chlorite. There are some indications that chlorine dioxide may be a primary product of these reactions just as it is when hypochlorite is used.

Action of Reducing Agents

Some reducing agents can also liberate chlorine dioxide from sodium chlorite under conditions where this salt alone is relatively stable. Such peculiar results are not limited to sodium chlorite. Turner, Nabar, and Scholefield (*43*) found that vat dyes in the reduced state promote the damage of cotton by hypochlorite.

The addition of formaldehyde to a solution of sodium chlorite causes the evolution of chlorine dioxide. Preliminary experiments indicate that in weakly acid solutions the chlorine dioxide evolution may be several times greater in the presence of formaldehyde than in its absence. Chlorate formation does not appear to be greatly affected. At about pH 7 chlorite alone in the solution undergoes scarcely any change in 6 hours at room temperature. On the addition of formaldehyde, the same concentration of sodium chlorite is almost completely consumed in 30 minutes with the formation of considerable quantities of chlorine dioxide and sodium chlorate. The invariable presence of carbon dioxide shows that formaldehyde is oxidized. The importance of this reaction at pH 7 is that it permits the production of chlorine dioxide in a solution under conditions where corrosion will be at a minimum and without the use of another oxidizing agent.

Formic acid does not cause this reaction but acetaldehyde, benzaldehyde, ferrous sulfate, etc., bring about evolution of chlorine dioxide. The mechanism of these reactions is unknown.

Chlorites can also react quantitatively with reducing agents. Their analytical determination depends upon the liberation of iodine from iodide. Bray (*4*) found also that iodates can be produced by the action of chlorites on iodine or iodides. Yntema and Fleming (*57*) suggested using this reaction for the determination of iodides. Jackson and Parsons (*19*) developed a method for the determination of sulfite by the use of sodium chlorite.

Action of Chlorites in Bleaching

Whether sodium chlorite or chlorine dioxide is the actual oxidizing agent in bleaching remains to be considered. Under certain conditions the consumption of sodium chlorite in acid solution was found to be 26 per cent in the absence of paper pulp and 80 per cent in its presence. The experiments using variations in the aeration of the acid solutions of chlorites showed that the quantity of chlorine dioxide formed was not increased by its removal from the sphere of action. If the chlorine dioxide formed from the chlorite had been exhausted in bleaching the paper pulp, additional quantities corresponding to the chlorite consumed would not be formed. Therefore, the majority of the consumption of the chlorite in the presence of paper pulp must have been by direct reaction of the chlorite ion. As pH 4 or higher is generally used for bleaching, the un-ionized chlorous acid need not be considered as a possible oxidizing agent. Chlorinated products derived from the material being bleached cannot be produced by a side reaction when chlorites are used, since chlorine cannot be formed from chlorites under the conditions of bleaching.

The results of Jeanes and Isbell (*21*) when oxidizing glucose to gluconic acid with sodium chlorite point to this same conclusion. They found that sodium chlorite and acid oxidized about four times as much glucose in one day as a similar quantity of chlorine dioxide in one week. The probable pH of the chlorine dioxide solution makes comparison at pH 4 the most accurate. It is possible that the oxidation accomplished by the chlorine dioxide depended upon its hydrolysis to chlorous acid.

On standing at room temperature in both brown and clear glass containers, solutions of chlorine dioxide in water become progressively more acid, which may be the result of hydrolysis. While the analyses of these solutions did not fully agree, they indicated chloric acid formation amounting to several per cent of the chlorine dioxide. The various combinations of titrations from which chlorous acid could be calculated gave contradictory results.

Acid solutions of chlorites have been found to bleach cellulosic materials without damage to the strength properties. The viscosity of cellulose solutions in cuprammonium hydroxide, a more sensitive measure of cellulose degradation than the conventional strength tests, also shows no change as the result of using acid chlorites.

In their experiments on glucose Jeanes and Isbell (*21*) found that chlorites can oxidize only the reducing sugars. If the terminal active oxygen atom is linked to two carbon atoms, as in cellulose chains, oxidation does not take place. Only minute traces of two- and four-carbon atom residues were found on oxidizing glucose; chlorites, therefore, do not attack the carbon-to-carbon bond to any appreciable extent. Hypochlorite, on the contrary, breaks the glucose molecule into many short-chain residues. In the degradation of cellulose, according to a current theory, the breaking of the carbon-to-carbon bond on one side of the anhydroglucose ring precedes rupture of the chain. The superiority of chlorite as a bleaching agent appears, therefore, to be based upon sound theoretical grounds.

No complete explanation can be constructed for the case of bleaching with a mixture of a chlorite and a hypochlorite. The results as measured by the strength properties of the bleached materials are intermediate between those customarily obtained by the use of a hypochlorite and of a chlorite in acid solution. The chief advantage of using both reagents is less corrosion by the bleaching medium compared with the effect of acid and chlorites. The experimental study of the mechanism of this bleaching process is incomplete, and while certain phenomena could be explained if chlorine dioxide were assumed to be an active bleaching agent, other observations indicate that it could not produce the results attained. Until these contradictions are resolved, the relative effect of the various components in the mixed solution cannot be evaluated.

The customary consideration of only the cellulose in its bleaching problems is unfortunate. In bleaching cellulose with hypochlorites, it is necessary to strive to preserve the cellulose. Chlorites act primarily on the materials sought to be removed in the bleaching process and not on the cellulose. The problem of bleaching cotton with chlorites then becomes different from that of wood pulp, and the methods for the most economical use of chlorites as bleaching agents may be different for these two materials.

Other Oxidations with Chlorites

There are many other oxidations in which a chlorite may be of advantage. Its oxidizing action is moderately strong and it can be used in acid solution. According to Groggins (*18*), the oxidation of isoeugenol to vanillin by dichromates or permanganates is difficult to control. Chlorites might suitably replace stronger oxidizing agents and make the reaction easier to control. When chlorates and acid are used as suggested by Milas (*33*, *53*), the evolution of chlorine dioxide frequently becomes excessive and violent explosions may result. It is quite possible that the oxidizing power of chlorites might be applied under milder conditions so that the chlorine dioxide evolution could be more easily controlled. The use of chlorites for the oxidation of only certain groups should be investigated.

Chlorine Dioxide from Chlorites

An important reaction of sodium chlorite is for the generation of chlorine dioxide. There are many suggested laboratory and commercial uses for this gas in the extensive literature. Chlorine dioxide is best prepared from chlorine and a chlorite solution. The evolution of chlorine dioxide is readily controlled by regulating the flow of chlorine. Logan (*29*) designed an apparatus which prevents chlorine from contaminating the chlorine dioxide generated. In this apparatus the chlorine is absorbed in a generator completely filled with chlorite solution. The solution is transferred to an aerator, and the chlorine dioxide is removed for use by aspirating with an inert gas. Accumulation of a dangerous concentration of gaseous chlorine dioxide is avoided in this generating apparatus.

Uses of Chlorites

Chlorites are finding varied uses in many fields. Processes using chlorites for the bleaching of wood pulp (*41*, *50*, *55*) and cotton and rayon textiles (*11*, *49*, *51*, *52*) are in commercial operation. The laboratory and some plant-scale information has already been published, chiefly in the papers mentioned. Studies on the treatment of many other materials with chlorites are in various stages of development from laboratory to commercial operation. In the cellulose field these include, for example, improving the quality of cotton linters, bleaching rag pulp with smaller amounts of chemicals, and bleaching straw. Both sodium chlorite and the easily controlled quantities of chlorine dioxide which can be produced from it are finding use in many other fields such as bleaching sugar sirups, treating starch, and improving the quality of flour. Not only does the use of chlorites result in the desired oxidation or bleaching, but it also yields a product whose other properties are superior. It has repeatedly been found that chlorites serve these purposes accompanied by such advantages as fewer steps in the process, shorter time, and smaller quantities of available chlorine (iodine equivalents).

It is obviously impossible to consider all these various developments in detail. Of those which have reached the commercial stage, only the bleaching of wood pulp and textiles will be discussed here. The bleaching of sugar sirups will serve as an example of the successful use of chlorite in plant-scale tests.

Bleaching of Wood Pulp

Wood pulp prepared by the sulfite process was fairly easily bleached to meet the demands existing two or three decades ago. Economic considerations and the exhaustion of readily available sources of suitable wood caused the pulp industry to move toward the southern states. The woods in this region were made into pulp by the kraft or sulfate process, and could serve as a source of the better grades of paper only if the pulp could be bleached. Years of study have been expended on the bleaching of this pulp, and the results have been applied to kraft pulps no matter where they are prepared.

The general process of bleaching such pulps requires treatment with various chemicals in several different steps. In the first step it is customary to use chlorine which reacts with residual lignin in the pulp to produce a soluble product. An alkaline treatment frequently follows to remove more of the colored impurities. Hypochlorite is then used, whether or not the pulp has been given an alkaline treatment, to oxidize the remaining colored bodies. This was a fairly satisfactory process if the bleaching was not carried too far. Previous to the present emergency the demand for whiter and whiter pulps led to the use of two stages of hypochlorite treatment which was superior to attempting to secure the improved color by a single stage of hypochlorite bleaching. However the hypochlorite was used, the more complete bleaching of the pulp was accompanied by a serious loss of strength. The most important strength tests in general use are the Mullen, or bursting, strength and the tearing resistance. The use of chlorites permits this thorough bleaching without lowering these strength properties of a pulp.

In most applications to wood pulp, all the bleaching that can safely be accomplished with the other chemicals is realized and followed by the chlorite treatment. Whether acid or hypochlorite is used with the chlorite depends upon the apparatus available and the specific results desired. Both processes have been used on wood pulp. The degree of improvement over other bleaching methods, when using chlorite and hypochlorite mixtures, depends to a great extent upon local conditions. The results with acidified chlorites are limited only by the quality of the pulp.

We are permitted to present some of the results obtained by one manufacturer with the acidified chlorite process for bleaching kraft pulp. One stage of hypochlorite bleaching was formerly used as the final step in their process. An additional stage using 0.5 per cent available chlorine (iodine equivalents) of sodium chlorite based upon the weight of the pulp at pH 4.5 has been introduced, which permits reduction of the amount of hypochlorite in the next previous bleaching stage. The use of chlorite produced the following changes in the properties of the resulting paper:

	Without Chlorite	With Chlorite	Advantage
Mullen strength	80%	90%	+12%
Tearing strength	100	150	+50

These figures represent the strength in pounds divided by the weight of a ream of paper of a certain size multiplied by 100 to convert to percentage. The process using chlorite produced a pulp of greater uniformity, and there was consequently less "below standard" production. The color of the bleached pulp was improved without any loss of strength.

Finishing Textiles

Chlorites are being used in various ways in the finishing operations of cotton and rayon textiles. The fabric as received by the finishing plant from the looms of the throw mill is known as greige goods. The cotton fabric in this unfinished form is water repellent and discolored, due to naturally occurring waxes, pectins, and color bodies in the raw fiber. In addition, a sizing, principally starch, applied to the warp threads to facilitate the weaving operation, is present.

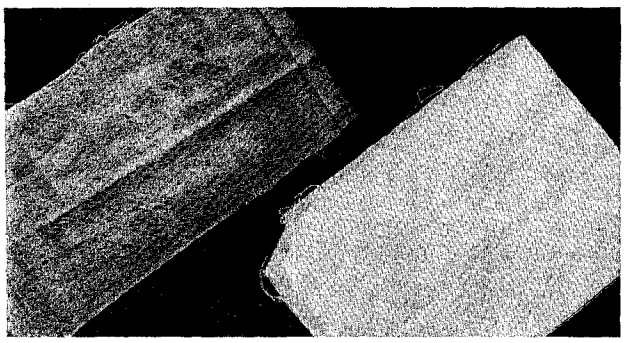

FIGURE 3. TEST FOR OXYCELLULOSE

The principal operations in the finishing plant to purify the cotton fabric and prepare it for subsequent processes are kier boiling with a caustic soda solution, followed by bleaching with a hypochlorite solution. Sodium chlorite is being used to advantage in both of these steps. When added to the kiering solution (*11*), it acts as a desizing agent and in addition as an aid to the caustic soda in dissolving and removing both the other water-repellent materials and the seed hull fragments known in the industry as motes. In the bleaching step a mixture of chlorite and hypochlorite (*52*) is displacing hypochlorite solution or "chemic" to advantage, with less degradation of the cellulose.

Various tests are generally associated with degradation of the cellulose. The viscosity or fluidity of the solution in cuprammonium hydroxide already mentioned has consistently shown the superior quality of the material prepared by the use of chlorite. Samples of the same brightness (whiteness) prepared by various treatments were submitted by a textile finishing company to the National Bureau of Standards without any marks to indicate the treatments used. The bureau confirmed previous findings that the sample bleached by the process, using a mixture of chlorite and hypochlorite, was superior to those bleached by the customary hypochlorite method or by peroxide.

Degradation of the cellulose may also be measured by an unstandardized test in which the reduction of silver nitrate is used as a visual indication of the presence of oxycellulose. Figure 3 was prepared from an unretouched photograph of the results of this test. The white cloth was bleached with the mixture of chlorite and hypochlorite; the other piece of cloth was bleached with hypochlorite alone, and its darker color shows that oxycellulose was formed during bleaching.

Spun rayon, pigmented rayon, and acetate rayon fabrics are scoured and bleached in a single operation by the action of a hot acid chlorite solution to which is added a detergent capable of functioning in an acid medium and resisting the oxidizing action of the chlorite (*11*). This not only saves time and cost by reducing the number of processing steps but also results in a more even "prepare" to promote more uniform dyeing.

Other uses for chlorites in the textile industry include the oxidation of vat dyes, the stripping of sulfur dyes, and the solubilizing of starch in weaving and finishing operations.

Sodium chlorite is also used in treating other materials than cellulose. Recently completed plant-scale tests used mixtures of sodium chlorite and calcium hypochlorite for the bleaching of sugar sirups. In present practice calcium hypochlorite is but one of several steps in the processing of the sugar sirups. The use of the mixture of sodium chlorite with the calcium hypochlorite yielded sirups of lighter and more uniform color than the customary process with hypochlorite alone in the bleaching step. Cost figures indicate that the new process is cheaper, partially because there is less loss.

Acknowledgment

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SULFAMIC ACID • • • • • An Industrial Review

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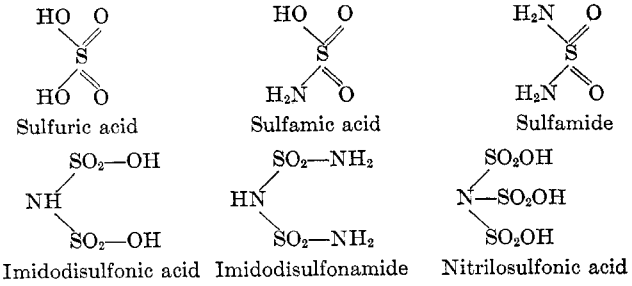
FOR many years sulfamic acid was known as an obscure laboratory chemical which possessed some rather unusual properties of interest only to scientific investigators. Considerable fundamental information concerning its physical and chemical properties was therefore already available when a new and practical process for its manufacture was discovered (*14*). During the four years which have followed the announcement of this new process, the commercialization of sulfamic acid has rapidly expanded, and today this former curiosity is being produced on a commercial scale and is now available in carload quantities. The purpose of this paper is to review briefly the chemistry of sulfamic acid and its derivatives and to discuss a number of industrial applications for them.

Audrieth and his students (*2*) published an excellent review of the chemistry of sulfamic acid and related aquo-ammonosulfuric acids. Some of the data which follow were taken from it and from the literature in general. The relationships of sulfamic acid with both the inorganic and organic fields of chemistry are presented in Table I and as follows:



The chemical structure of sulfamic acid as the half amide of sulfuric acid is here brought out. Replacement of both hydroxyl groups of sulfuric acid with amide groups yields sulfamide. Sulfonation of sulfamic acid yields imidodisulfonic acid, and a third sulfonic acid substitution yields nitrilosulfonic acid. Both the imido- and the nitrilosulfonic acids are unstable in the free acid condition and are rapidly hydrolyzed into sulfamic acid which is known to be comparatively stable in aqueous solutions at ordinary temperatures. The salts of these acids, similar to the sulfamates, are comparatively stable in neutral or alkaline solutions. Upon alkaline hydrolysis, sulfamide yields ammonia and the corresponding sulfamate.

Table I. Mixed Aquo-ammono Acids

Related to Sulfuric Acid		Related to Carbonic Acid	
Formula	Name	Formula	Name
$HO—SO_2—OH$	Sulfuric acid	$HO—CO—OH$	Carbonic acid
$HO—SO_2—NH_2$	Sulfamic acid	$HO—CO—NH_2$	Carbamic acid
$H_2N—SO_2—NH_2$	Sulfamide	$H_2N—CO—NH_2$	Carbamide (urea)
$HN(SO_2—NH_2)_2$	Imidodisulfonamide	$HN(CO—NH_2)_2$	Biuret
$NH(SO_2—OH)_2$	Imidodisulfonic acid	$HN(CO—OH)_2$	Imidodicarbonic acid

Table I illustrates the relation between the nitrogen-substituted sulfuric acid and the nitrogen-substituted carbonic acid series.

While this tabulation illustrates the relationships in structure and composition, the chemical relationships also hold quite well if the greater stability of the sulfuric acid series is taken into consideration. For example, carbamic acid and the carbamates are easily hydrolyzed while sulfamic acid and the sulfamates are comparatively stable.

Physical and Chemical Properties

The more important properties upon which, in most instances, the industrial uses of sulfamic acid are based are as follows: It is a solid melting at 205° C.; it is colorless,