# DICHLORINE MONOXIDE, HYPOCHLOROUS ACID, AND HYPOCHLORITES

## 1. Introduction

Chlorine has formal positive oxidation numbers (states) in oxychlorine compounds since its appreciable electronegativity (2.83) on the Allred-Rochow scale is exceeded by that of oxygen. All positive chlorine compounds are strong oxidants because the transfer of electrons to the orbitals of electronegative chlorine is favored in reactions with compounds of less electronegative elements. Chlorine oxides and oxo-acids exhibit the lack of stability expected of compounds having bonds between two strongly electronegative elements. The decomposition reactions of these compounds are, therefore, always energetic and violent in many cases (Table 1). The chemical properties of chlorine oxides and oxo acids display a trend toward greater thermodynamic and kinetic stability with increasing oxidation state. It is possible to isolate pure perchloric acid and its anhydride, $Cl_2O_7$, whereas pure hypochlorous, chlorous, and chloric acids have not been obtained. The reduction potentials of the oxo acids exhibit a similar trend in that the strongest oxidants have chlorine in its lower states of oxidation. Compounds of chlorine having intermediate oxidation states exhibit a strong tendency to disproportionate.

The oxo anions of chlorine are weaker oxidants than the corresponding acids. Because they are also more stable, it is not too difficult to isolate certain salts of those acids that can be obtained only in aqueous solution. Hypochlorites and chlorites are hydrolyzed in aqueous solution since HOCl and $HClO_2$ have

Table 1. **Chlorine Oxides[a] and Oxo Acids**

| Formula | CAS Registry number | Oxidation state | Stability |
|---|---|---|---|
| | | | *Oxides* |
| $Cl_2O$ | [7791-21-1] | +1 | anhydride of HOCl; yellowish brown gas at 25°C; explodes when heated or sparked |
| $Cl_2O_2$ | [12292-23-8] | +2 | $t_{1/2}$ of gas = 4.8 day at −78°C |
| $Cl_2O_3$ | [17496-59-2] | +3 | anhydride of $HClO_2$; explodes below 0°C |
| $ClO_2$ | [10049-04-4] | +4 | odd electron molecule; yellow gas; explodes at >6.7 kPa[b] |
| $Cl_2O_4$ | [27218-16-2] | +1,+7 | pale yellow liquid; decomposes to $Cl_2$, $O_2$, and $Cl_2O_6$ |
| $Cl_2O_6$ | [12442-63-6] | +6 | red liquid; gas decomposes to $Cl_2O_4 + O_2$ |
| $Cl_2O_7$ | [12015-53-1] | +7 | anhydride of $HClO_4$; colorless liquid; can be distilled under reduced pressure |
| | | | *Acids* |
| HOCl[c] | [7790-92-3] | +1 | very weak acid, p$K_a$ 7.54; cannot be concentrated |
| $HClO_2$ | [13898-47-0] | +3 | decomposes rapidly at 25°C; p$K_a$ ~2.0; cannot be concentrated |
| $HClO_3$ | [7790-93-4] | +5 | decomposes slowly at ~40% and 25°C; cannot be concentrated |
| $HClO_4$ | [7601-90-3] | +7 | can be concentrated |

[a] Anhydride of chloric acid, $Cl_2O_5$, is unknown. Oxides with even number of oxygen atoms are mixed anhydrides. Other chlorine oxides such as the radicals ClO, $ClO_3$, and $ClO_4$ are known. Chlorine monoxide [14989-30-1], ClO plays a key role in depletion of the ozone layer.

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] The isomeric HClO is an unstable compound formed in the earth's ozone layer.

acid dissociation constants of $\sim 10^{-8}$ and $10^{-2}$, respectively; however, aqueous chloric and perchloric acids are fully ionized.

The chlorine oxides are anhydrides or mixed anhydrides of chlorine oxo acids; oxides with an odd number of oxygens are simple anhydrides whereas those with an even number are mixed anhydrides.

Chlorine in dichlorine monoxide, hypochlorous acid, and ionic hypochlorites is in the + 1 formal oxidation state. Other compounds where univalent chlorine is bonded to oxygen are the alkyl, aryl, and acyl hypochlorites and other unipositive chlorine compounds such as $ClOSF_5$, $ClOSO_2F$, ClONO, $ClONO_2$, and $ClOClO_3$. The latter compounds are chlorine derivatives of the corresponding acids and can also be considered as mixed anhydrides of HOCl and the corresponding acid. The polar bonding in these compounds imparts a partial positive charge on the first chlorine atom. Along with HCl, $ClONO_2$ forms a temporary chlorine reservoir in the upper stratosphere that reduces depletion of the ozone layer. The compound HOCl is also an important intermediate in the chemistry of the stratosphere.

## 2. Dichlorine Monoxide

Dichlorine monoxide is the anhydride of hypochlorous acid; the two compounds are interconvertible in the gas and aqueous phases via the equilibrium:

Table 2. **Gas–Liquid–Solid Properties of Dichlorine Monoxide**

| | |
|---|---|
| color (gas, liquid, solid) | yellow-brown, red-brown, cherry-red |
| density (solid) | 2.089 g/cm$^3$ at 90 K (1) |
| freezing point | −120.6°C (2) |
| boiling point | 2.0°C (3) |
| vapor pressure (173–288 K) | $\log P$ (kPa) = 6.995 − 1373T$^{-1}$ (3) |
| solubility (g/100 g $H_2O$) at −9.4°C | 143.6 (2) |

$Cl_2O + H_2O \rightleftharpoons 2\ HOCl$. Like other chlorine oxides, $Cl_2O$ has an endothermic heat of formation and is thus thermodynamically unstable with respect to decomposition into chlorine and oxygen. Dichlorine monoxide typifies chlorine oxides in being highly reactive and potentially explosive. Nevertheless, it can be handled safely with proper precautions.

**2.1. Properties.** *Gas–Liquid–Solid.* Physical properties of gaseous, liquid, and solid dichlorine monoxide are summarized in Table 2. Dichlorine monoxide crystallizes in the tetragonal crystal system (1). It readily dissolves in water to give a solution of hypochlorous acid containing a small equilibrium concentration of $Cl_2O$. A saturation solution at −9.4° is equivalent to 71% HOCl.

*Vapor–Liquid Equilibria.* Henry's constant for the gas–liquid equilibrium: $Cl_2O(aq) \rightleftharpoons Cl_2O(g)$ at 3.46°C is $H = 14.23$ kPa $m^{-1}$ (4).

*Solvent Extraction.* Carbon tetrachloride ($CCl_4$) extracts chlorine monoxide but not HOCl from concentrated HOCl solutions. The partition coefficient at 0°C for the equilibrium $Cl_2O(aq) \rightleftharpoons Cl_2O(CCl_4)$ is 2.22 (5,6).

*Thermodynamic Data.* Thermodynamic values for dichlorine monoxide are tabulated in Table 3.

*Spectral Data.* Microwave spectroscopic measurements show $Cl_2O$ to be a nonlinear molecule with $C_{2v}$ symmetry (8). The ultraviolet (uv) spectrum shows a maximum near 260 nm with absorptivity of 511 $M^{-1}$ cm$^{-1}$ (9). The infrared (ir) spectrum shows three fundamental bands at 300, 642, and 687 cm$^{-1}$ (10).

**2.2. Chemistry.** *Explosivity.* Explosion of gaseous dichlorine monoxide can be initiated by spark or heat. The liquid is shock sensitive but less so than $ClO_2$ (11). The minimum explosive concentration of gaseous $Cl_2O$ in oxygen at 23°C and 101 kPa (1 atm) in faint daylight is 23.5 mol% (12). Explosions are mild in the 25–30% range but become progressively more violent at higher concentrations. The effect of various diluent gases on the explosion limit at various total pressures has been determined in the complete absence of light. The extrapolated explosion limit in $O_2$ is ~33 mol% (13). The threshold for spark initiated decomposition of pure $Cl_2O$ is 0.53 kPa (4.0 Torr).

Table 3. **Thermodynamic Values for Gaseous $Cl_2O^a$**

| | |
|---|---|
| heat of solution in $H_2O$: $\Delta H_{soln}$ | 36.6 kJ mol$^{-1}$ (4) |
| heat of vaporization: $\Delta H_{vap}$ | 26.3 kJ mol$^{-1}$ |
| heat of formation: $\Delta H_f^\circ$ | 80.3 kJ mol$^{-1}$ |
| free energy of formation: $\Delta G_f^\circ$ | 97.9 kJ mol$^{-1}$ |
| entropy: $S^\circ$ | 266.2 J K$^{-1}$ mol$^{-1}$ |
| heat capacity: $C_p$ | 45.4 J K$^{-1}$ mol$^{-1}$ |

[a] Ref. 7.

*Thermal and Photolytic Decomposition.* Dichlorine monoxide decomposes thermally and photochemically into $Cl_2$ and $O_2$. Gaseous $Cl_2O$ decomposes thermally in 12–24 h at 60–100°C, but at 150°C the reaction is complete in only a few minutes; above 110°C the reactions terminate in explosion (14). The decomposition is preceded by an induction period inversely proportional to the starting $Cl_2O$ concentration. Several mechanisms, some involving chains, have been proposed for this heterogeneous reaction (15). The photolytic decomposition, initiated by cleavage into ClO, O, and Cl free radicals, is sensitized by $Cl_2$ (16). Significant concentrations of $ClO_2$ are generated from $Cl_2O$ by controlled thermal decomposition or irradiation of $CCl_4$ solutions. Photolysis of matrix-isolated $Cl_2O$ yields ClClO, $(ClO)_2$, and ClO (17).

*Inorganic Reactions.* Dichlorine monoxide reacts with a variety of inorganic substances. The reaction of $Cl_2O$ with various free radicals (F, Cl, Br, O, N, and OH) has been studied kinetically (18). Some reactions of $Cl_2O$ with inorganic compounds are summarized in Table 4. The low temperature, condensed phase reaction with $N_2O_5$ is a convenient route to $ClNO_3$ (22). In solution or in the gas phase both $ClNO_2$ and $ClNO_3$ are formed. Chlorine dioxide is an intermediate in certain reactions of $Cl_2O$ as in the preparation of chloryl fluoride and in the formation of ionic complexes from $SO_3$ and $AsF_5$ (21). The transformation of metal halides into oxy halides by $Cl_2O$ apparently involves hypochlorite intermediates (26). Dichlorine monoxide can be used for generation of singlet oxygen in the chemical oxygen iodine laser (COIL) (27).

Dichlorine monoxide reacts explosively with ammonia forming nitrogen, chlorine, and water (28). It also reacts with $Ca(OH)_2$ and moist CaO forming

Table 4. **Reactions of $Cl_2O$ with Inorganic Compounds**

| Reaction | Reference |
|---|---|
| $Cl_2O + 3\ F_2 \xrightarrow{\text{CaF},-78^\circ\text{C}} ClF_3O \underset{>80\%}{+} ClF_3$ | 19 |
| $2\ Cl_2O + AgF_2 \xrightarrow{65-70^\circ\text{C}} ClO_2F + AgF + 3/2Cl_2$ | 20 |
| $5\ Cl_2O + 3\ AsF_5 \xrightarrow{-78\text{ to }-50^\circ\text{C}} 2\ ClO_2AsF_6 + AsOF_3 + 4\ Cl_2$ | 21 |
| $Cl_2O + N_2O_5 \xrightarrow{0^\circ\text{C}} 2\ \underset{90\%}{ClNO_3}$ | 22 |
| $4\ Cl_2O + 3\ SO_3 \xrightarrow{CFCl_3,-27^\circ\text{C}} (ClO)(ClO_2)[S_3O_{10}] + 3\ Cl_2$ | 21 |
| $Cl_2O + TiBr_4 \longrightarrow TiOBr_2 + Br_2 + Cl_2{}^a$ | 24 |
| $3\ Cl_2O + 2\ BCl_3 \xrightarrow{-78^\circ\text{C}} B_2O_3 + 6\ Cl_2{}^b$ | 23 |
| $2\ Cl_2O + P(NCl_2)_3 \longrightarrow PO_2Cl + 3\ NCl_3$ | 25 |

[a] Similar reactions occur with $TiCl_4$, $SnBr_4$, $SnCl_4$, and $PbCl_4$, (26).

[b] $AlBr_3$ similarly gives $Al_2O_3$, but with $AlCl_3$ there is no reaction.

calcium hypochlorite (29,30). Dry hypochlorites are oxidized to chlorates by $Cl_2O$. Extraction of $CCl_4$ solutions of $Cl_2O$ with aqueous solutions or suspensions of alkali and alkaline earth metal hydroxides and evaporating the extract under vacuum at 40–50°C gives pure anhydrous or hydrated hypochlorites (31).

Dichlorine monoxide exists in very low equilibrium concentrations in dilute HOCl solutions, nevertheless, it is a kinetically significant reactant. For example, although tetracyanonickelate(II) can be oxidized by chlorine in aqueous solution to *trans*-$Ni^{III}(CN)_4(H_2O)_2^-$, the second-order rate constant at 25°C for oxidation with $Cl_2O$ is 40 times greater than for $Cl_2$ and $2.6 \times 10^7$ greater than for HOCl (32).

*Organic Reactions.* Dichlorine monoxide reacts primarily as a chlorinating agent toward organic matter. By contrast with chlorine, which forms HCl as a by-product, dichlorine monoxide forms water. Although HOCl is an intermediate by-product, it is a reservoir of $Cl_2O$ via the equilibrium: $2\ HOCl \rightleftharpoons Cl_2O + H_2O$.

*Reaction with Aliphatics.* Methane is quantitatively converted to $CCl_4$ by reaction with dichlorine monoxide at 350°C (33). Lower temperatures give a mixture of chlorinated methanes. The gas-phase reaction of propane with $Cl_2O$ at 100°C gave 1- and 2-chloropropane (7:1 molar ratio) and HOCl (34). The liquid-phase reaction with saturated compounds produces 2 mol of chlorinated products per mol substrate: $2\ RH + Cl_2O \rightarrow 2\ RCl + H_2O$. The photoinduced reaction proceeds via a free-radical chain mechanism, giving a mixture of chlorination products (35). In contrast, the dark reaction favors tertiary chlorination (36). Dichlorine monoxide is more selective than chlorine but less selective than *tert*-butyl hypochlorite (35).

Reaction with olefins involves initial addition of $Cl_2O$. Trichloroethylene gave $Cl_3CCHCl_2$, $Cl_3CCHO$, and $(Cl_3CCHCl)_2O$ (37). By contrast, reaction of $Cl_2O$ with cyclohexene forms 2-chlorocyclohexene (40% yield) and 2-chlorocyclohexanol (27% yield) as the main products (37). Dichlorine monoxide has been postulated as an intermediate in the addition of HOCl to olefins (38).

Reaction of $Cl_2O$ with primary amines forms *N,N*-dichloro derivatives (39). Dichlorine monoxide in $CCl_4$ solution reacts with acetic acid forming acetyl hypochlorite (40). Generated in situ in the presence of $CCl_4$ by reaction of $CO_2$ and NaOCl, it has been used in preparation of substituted hydrazines (41). Dichlorine monoxide reacts with $COF_2$ in the presence of CsF to give $CF_3OCl$ (42).

*Reaction with Aromatics.* Dichlorine monoxide is a powerful and selective reagent for either ring or side-chain chlorination of deactivated aromatic substrates providing excellent yields under mild conditions where conventional reagents fail or require harsh conditions (43). For example, *p*-nitrotoluene in $CCl_4$ at 25°C undergoes side chain chlorination by $Cl_2O$ giving trichloromethylnitrobenzene in 100% yield.

$$2\ CH_3C_6H_5NO_2 + 3\ Cl_2O \longrightarrow 2\ CCl_3C_6H_5NO_2 + 3\ H_2O$$

The reaction proceeds by a free-radical mechanism involving hydrogen abstraction by ClO radicals. The strong electrophilicity of $Cl_2O$ was further demonstrated in studies using *p*-xylene as the substrate. The specific reactivity of

$Cl_2O$ for monohalogenation was equivalent to $Cl_2$ and 220 times greater than that of $Br_2$. By contrast, the reactivity of HOCl was insignificant (44).

By contrast to the thermal reaction, *p*-nitrotoluene undergoes ring polychlorination in >95% yield by $Cl_2O$ at 25°C under the influence of strong protic acids via a proposed electrophilic aromatic substitution mechanism (43).

$$2\ \mathrm{CH_3C_6H_5NO_2} + n\ \mathrm{Cl_2O} \longrightarrow 2\ \mathrm{CH_3C_6H_{4-\mathit{n}}Cl_\mathit{n}NO_2} + n\ \mathrm{H_2O}$$

Reaction of $Cl_2O$ with phenol in $CCl_4$ solution forms *o*-chlorophenol and *p*-chlorophenol in 65 and 22% selectivity, respectively (45). By contrast, anisole gives *o*-chloroanisole and *p*-chloroanisole in 26 and 54% selectivity, respectively. Dichlorine monoxide is also a probable intermediate in the chlorination of anisole by HOCl (46). Quinones undergo monochlorination by $Cl_2O$ at the 2-position, except in the case of benzoquinone, which gave 2,5-dichlorobenzoquinone (47).

*Reaction with Heterocyclics.* Dichlorine monoxide reacts with finely divided cyanuric acid in a fluidized bed forming dichloro- and trichloroisocyanuric acids (48) and with monosodium cyanurate monohydrate yielding sodium dichloroisocyanurate monohydrate (49). (see CYANURIC AND ISOCYANURIC ACIDS). Ammelide and ammeline are also converted to trichloroisocyanuric acid by dichlorine monoxide; the exocyclic amino groups being converted to $NCl_3$ (50).

**2.3. Preparation.** *Laboratory Scale.* Methods are available for preparation of gaseous or liquid $Cl_2O$ as well as organic solutions.

*Chlorination of HgO.* Gaseous dichlorine monoxide is conveniently generated by passing chlorine gas through mercuric oxide in a packed tubular reactor:

$$2\ \mathrm{Cl_2} + 2\ \mathrm{HgO} \longrightarrow \mathrm{Cl_2O} + \mathrm{HgO}\cdot\mathrm{HgCl_2}$$

High yields are favored by cooling the reactor, diluting the chlorine with an inert gas, and mixing the dry HgO with an inert material, eg, sand (33,51). Use of excess HgO ensures complete conversion of chlorine. The spent HgO can be regenerated by treatment with aqueous caustic, filtering, washing with water, and drying at 110°C. The relatively pure $Cl_2O$ in the exit gases can be passed through a trap cooled with dry ice and acetone to condense liquid $Cl_2O$ (2). The preparation can also carried out under static conditions (52).

*Organic Solutions.* Gaseous $Cl_2O$ formed by the above reaction of $Cl_2$ and HgO can be passed into cold $CCl_4$ to prepare an organic solution. An organic solution of $Cl_2O$ can also be prepared by addition of HgO to a solution of $Cl_2$ in cold $CCl_4$ followed by filtration to remove the basic mercuric chloride. A dilute solution containing a few percent $Cl_2O$ is obtained in 90% yield and is stable when stored in the dark under refrigeration. Moist soda ash can also be used but the yield is reduced to ~40% (33).

*Surface Chlorination of NaOH.* Dichlorine monoxide is formed by passing chlorine diluted with an inert gas over the surface of a slowly stirred 50% NaOH solution at ~5°C. The exit gas also contains some unreacted chlorine as well as HOCl and small amounts of water vapor (53). Passage through $P_2O_5$ absorbs the moisture and dehydrates the HOCl to $Cl_2O$. Condensation of the

$Cl_2O$ separates it from the inert gas and most of the chlorine. Fractionation removes the last traces of chlorine.

*From HOCl Solutions.* Dichlorine monoxide can be prepared from concentrated HOCl solutions by vacuum distillation (5), stripping with air (54), and treatment with anhydrous $Ca(NO_3)_2$ (55).

*Industrial Scale.* Routes more amenable to commercial-scale production are based on reaction of chlorine with sodium bicarbonate, carbonate, or sesquicarbonate. For example, reaction of $Cl_2$ and water vapor with soda ash in a countercurrent tower reactor gives $Cl_2O$ mixed with $Cl_2$, HOCl, $H_2O$, and $CO_2$ (56). The reaction can also be carried out in a fluidized-bed reactor employing sodium sesquicarbonate (57). High yields of $Cl_2O$ are reported for the reaction of $Cl_2$, diluted with moist air, with porous soda ash (58). A continuous scheme for generating $Cl_2O$ involves reaction of $Cl_2$ with anhydrous soda ash in a fixed or fluidized-bed reactor at 180°C (59). The $Cl_2O$ can be used as is or absorbed in water to produce a hypochlorous acid solution. The $Cl_2O$-containing gas from reaction of atomized NaOH can be dried, condensed, and fractionated to obtain liquid $Cl_2O$ (60).

**2.4. Analysis.** *Iodometry.* Dichlorine monoxide can be quantitatively determined alone or in admixture with $Cl_2$, by iodometry; the acid consumed is a direct measure of $Cl_2O$ (61). The reactions involved are:

$$Cl_2O + H_2O \longrightarrow 2\ HOCl$$
$$2\ HOCl + 4\ I^- + 2\ H^+ \longrightarrow 2\ I_2 + 2\ Cl^- + 2\ H_2O$$
$$Cl_2 + 2\ I^- \longrightarrow I_2 + 2\ Cl^-$$

The liberated iodine is titrated with thiosulfate ($2\ S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\ I^-$) and the excess acid by sodium hydroxide. Hypochlorous acid reacts similarly to $Cl_2O$ and cannot be distinguished from it by wet analysis.

*Instrumental.* Gaseous mixtures of $Cl_2$, $Cl_2O$, and HOCl can be analyzed by mass spectrometry (62,63), by ir (10), or by uv spectrophotometry (9,63). Gas chromatography can be used to analyze mixtures of air, $Cl_2$, and $Cl_2O$ (52,64).

**2.5. Uses.** Dichlorine monoxide has been used as an intermediate in the manufacture of calcium hypochlorite and in sterilization for space applications (65) (see STERILIZATION TECHNIQUES). Its use in the preparation of chlorinated solvents (66) and chloroisocyanurates has been described. Dichlorine monoxide has been shown to be effective in bleaching of pulp (qv) and textiles (67). It also can be used as an etchant in semiconductor manufacture (68).

## 3. Hypochlorous Acid

Hypochlorous acid [7790-92-3] is a highly reactive and relatively unstable compound known both in solution and in the gas phase. In solution it is the most stable and the strongest of the hypohalous acids and is one of the most powerful oxidants among the chlorine oxy acids. Although it is not an item of commerce, it is an important intermediate in the manufacture of various inorganic and organic chemicals and also performs an important role as a disinfectant and oxidant in water treatment.

**3.1. Properties.** *Dissociation.* Hypochlorous acid is a very weak acid (an order of magnitude weaker than carbonic acid) as shown by the the dissociation equilibrium below.

$$\mathrm{HOCl} \leftrightharpoons \mathrm{H}^+ + \mathrm{ClO}^- \qquad K_a^{25^\circ\mathrm{C}} = 2.90 \times 10^{-8}\ M$$

The temperature (kelvin) dependence is given by $\mathrm{p}K_\mathrm{a} = 0.0253\mathrm{T} + 3000\mathrm{T}^{-1} - 10.0686$ (69): The calculated value of $pK_\mathrm{a}$ at 25° is 7.54. The dissociation energy of HOCl from the latter study is 16.3 kJ $\mathrm{mol}^{-1}$, which is in reasonable agreement with the value of 15.1 kJ $\mathrm{mol}^{-1}$ based on the heat of neutralization (70). The relative concentrations of HOCl and $\mathrm{ClO}^-$ are a function of pH. The HOCl fraction is given by: $[\mathrm{HOCl}]/([\mathrm{HOCl}] + [\mathrm{ClO}^-]) = (K_\mathrm{a}/[\mathrm{H}^+] + 1)^{-1}$.

*Phase Equilibria.* The phase diagram of aqueous HOCl-$\mathrm{Cl_2O}$ shows a eutectic at $-40^\circ$C (11.7 mol % $\mathrm{Cl_2O}$) (2). Below the eutectic concentration the solid phase in equilibrium with the liquid phase is ice and at higher concentrations the solid phase is $\mathrm{HOCl \cdot 2\ H_2O}$. Liquid $\mathrm{Cl_2O}$ and aqueous HOCl are only partially miscible. Mixing stoichiometric amounts of $\mathrm{Cl_2O}$ and water does not give pure HOCl but results instead in separation of two liquid phases, which on freezing give the solid compound $\mathrm{HOCl \cdot 2H_2O}$.

*Solvent Extraction.* Hypochlorous acid can be extracted from aqueous solution by polar solvents such as ketones, esters, and nitriles (71).

*Vapor–Liquid Equilibria.* Hypochlorous acid and dichlorine monoxide coexist in the liquid and vapor phase. Dilute HOCl solutions are colorless; at higher concentrations the color ranges from yellow to yellow-orange due to small equilibrium amounts of $\mathrm{Cl_2O}$. At 0°C a 5% ($\sim$1 $m$) solution contains $\sim$0.03% $\mathrm{Cl_2O}$ and a 25% ($\sim$6.5 $m$) solution contains $\sim$1% $\mathrm{Cl_2O}$ (6). Vapor pressure measurements of aqueous HOCl solutions show that HOCl is the main chlorine species in the vapor phase over $\leq$5% solutions, whereas at higher concentrations, $\mathrm{Cl_2O}$ becomes dominant (72). Data on the various equilibria involving HOCl and $\mathrm{Cl_2O}$ in the aqueous and gas phases are summarized in Table 5. The overall

Table 5. **Hypochlorous Acid Vapor–Liquid Equilibria**

| | |
|---|---|
| $2\ \mathrm{HOCl(aq)} \rightleftharpoons \mathrm{Cl_2O(aq)} + \mathrm{H_2O(l)}^a$ | $K_\alpha{}^{0^\circ\mathrm{C}} = 3.55 \times 10^{-3}$; $K_\alpha{}^{19^\circ\mathrm{C}} = 8.70 \times 10^{-3}\ m^{-1}$ |
| $\mathrm{HOCl(aq)} \rightleftharpoons \mathrm{HOCl(g)}$ | $K_\beta{}^{10^\circ\mathrm{C}} = 32.0^b, 34.7^c, K_\beta{}^{20^\circ\mathrm{C}} = 93.3^b, 65.3^{c,d}\ \mathrm{Pa}\ m^{-1}$ |
| $2\ \mathrm{HOCl(aq)} \rightleftharpoons \mathrm{Cl_2O(g)} + \mathrm{H_2O(l)}$ | $K_\gamma{}^{10^\circ\mathrm{C}} = 28.0^b, 82.6^e, K_\gamma{}^{20^\circ\mathrm{C}} = 86.6^b, 196.0^e\ \mathrm{Pa}\ m^{-2}$ |
| $2\ \mathrm{HOCl(g)} \rightleftharpoons \mathrm{Cl_2O(g)} + \mathrm{H_2O(g)}^f$ | $K^{25^\circ\mathrm{C}} = 1.45$ ka |

[a] Value at 19°C calculated by extrapolating 0°C value using estimated heat of hydration of $\mathrm{Cl_2O}$ $\sim$31.3 kJ $\mathrm{mol}^{-1}$ (6).

[b] Dynamic measurements on $\sim$0.15–2.7 $m$ aqueous HOCl (72).

[c] Dynamic measurements on aqueous NaOCl, values calculated using: $3.05 \times 10^9 \exp(-5172/\mathrm{T})$ Pa $M^{-1}$; dynamic measurements on 0.01–0.1 $M$ HOCl solutions at 50° gave $K_\beta = 370.6$ Pa $M^{-1}$ (73).

[d] Dynamic measurements at 20°C on 2–20 ppm av $\mathrm{Cl_2}$ at pH 5.5 gave $K_\beta$ (unitless) = 0.076 (137.3 Pa $m^{-1}$) for Henry's law constant (74); similar measurements on $\sim$5 ppm av $\mathrm{Cl_2}$ at pH $\sim$5.6 gave 0.0604 atm (110.1 Pa $m^{-1}$) (75).

[e] Static measurements on $\sim$1–20 $m$ aqueous HOCl at $\sim$3.5–20°C; by contrast to reference 72 calculations assume only $\mathrm{Cl_2O}$ present in gas phase (76).

[f] Measurements via mass spectrometry on equilibrated $\mathrm{HOCl/Cl_2O/H_2O}$ gaseous mixtures (62).

Table 6. **Thermodynamic Data for Hypochlorous Acid**[a]

| | Aqueous | Gas |
|---|---|---|
| $\Delta H_{\mathrm{neut}}$ (kJ mol$^{-1}$) | −15.1 (70) | |
| $\Delta H_f^\circ$ (kJ mol$^{-1}$) | −120.9 | −78.7 |
| $\Delta G_f^\circ$ (kJ mol$^{-1}$) | −79.9 | −66.1 |
| $S^\circ$ (kJ K$^{-1}$ mol$^{-1}$) | 142.3 | 236.7 |
| $C_p$ (kJ K$^{-1}$ mol$^{-1}$) | | 37.15 |
| $\mathrm{HOCl} + \mathrm{H}^+ + 2\,\mathrm{e}^- \rightarrow \mathrm{Cl}^- + \mathrm{H_2O}$ | $E^\circ = 1.49$ V | |

[a] Ref. 7.

agreement in the values of $K\beta$ and $K\gamma$ and their temperature dependence is not very good.

*Relative Volatility.* Hypochlorous acid is more volatile than water and aqueous solutions can be distilled to yield solutions of higher concentration. For dilute solutions, the relative volatility is given by $\alpha = \mathrm{HOCl}_v/\mathrm{HOCl}_a$, which is the ratio of the mol fraction of HOCl in the vapor and aqueous phases. The experimentally determined relative volatility for 0.06–2 m$M$ solutions of HOCl at 25°C is 2.74 (77), which yields a value of 156.0 Pa $M^{-1}$ for the equilibrium constant $K\beta$ via the relationship $K\beta = \alpha P_{\mathrm{H_2O}}/55.6$ where $P_{\mathrm{H_2O}}$ is the vapor pressure of water (Pa) and 55.6 is mols water/L. This is consistant with the value of 154.6 Pa $m^{-1}$ extrapolated from the data of (72) ($m = M/\mathrm{d}$ where $m$ is molality and $M$ is molarity and d is density; for dilute solutions $m \cong M$). See (78) for additional data on $\alpha$.

*Thermodynamic Data.* Enthalpy and free energy of formation, entropy, heat capacity, and reduction potential of HOCl are listed in Table 6.

*Spectral Data.* The uv spectrum of gaseous HOCl shows absorption bands at 240 and 310 nm with absorptivities of 58.4 and 16.3 $M^{-1}$ cm$^{-1}$ (9). The uv absorption spectrum of aqueous HOCl shows a maximum at 235 nm with absorptivity of 100 $M^{-1}$ cm$^{-1}$ (69). The ir spectrum of gaseous HOCl shows three fundamental absorption bands: 725, 1240, and 3587 cm$^{-1}$ (79). Microwave spectroscopy of HOCl in the vapor phase shows $d_{\text{O-H}} = 0.096$ nm, $d_{\text{Cl-O}} = 0.169$ nm, and $\angle$H-O-Cl $= 102.5^\circ$ (80). Hypochlorous acid closely resembles water in bond angle (104.7°) and O-H bond length (0.096 nm), and $\mathrm{Cl_2O}$ in Cl-O bond length (0.170 nm).

*Germicidal Activity.* The germicidal activity of aqueous chlorine is due primarily to HOCl. Although hypochlorite ion itself is a relatively poor disinfectant (81) in comparison to hypochlorous acid, it serves as a reservoir of the latter via the equilibrium: $\mathrm{ClO^-} + \mathrm{H^+} \leftrightharpoons \mathrm{HOCl}$. At 25°C, the ratio of $\mathrm{ClO^-}$/HOCl is 0.50 at pH 7.54. The efficiency of inactivation is affected by pH, temperature, time of contact, and type and concentration of organisms (82). The mode of action with bacteria involves diffusion through the cell wall followed by reaction with the enzymatic system. In swimming pools, the presence of cyanuric acid reduces the bactericidal effectiveness of HOCl by formation of chloroisocyanurates (83).

**3.2. Chemistry.** *Stratospheric.* The primary source of HOCl in the stratosphere is the gas-phase reaction (84):

$$\mathrm{HO_2} + \mathrm{ClO} \longrightarrow \mathrm{HOCl} + \mathrm{O_2} \qquad k^{25^\circ\mathrm{C}} = 3.0 \times 10^9\ M^{-1}\mathrm{s}^{-1}$$

HOCl is rapidly photolyzed by solar uv radiation producing HO and Cl radicals. Although these radicals can decompose HOCl, the rates are much slower than HOCl photolysis. However, these radicals can decompose ozone.

$$\mathrm{HOCl} + h\nu \longrightarrow \mathrm{HO} + \mathrm{Cl}$$

$$\mathrm{HOCl} + \mathrm{Cl} \longrightarrow \mathrm{HO} + \mathrm{Cl_2} \qquad k^{25^\circ\mathrm{C}} = 1.1 \times 10^9 M^{-1}\mathrm{s}^{-1}\ (85)$$

$$\mathrm{HOCl} + \mathrm{HO} \longrightarrow \mathrm{H_2O} + \mathrm{ClO} \qquad k^{25^\circ\mathrm{C}} = 3.3 \times 10^8 M^{-1}\mathrm{s}^{-1}\ (84)$$

The estimated photolysis lifetime of ~2 h (at 30 km) suggests that HOCl may be unimportant as a reservoir for stratospheric chlorine (63). HOCl is also an intermediate in activation of chlorine reservoirs via its heterogeneous formation and decomposition in aerosols present in stratospheric clouds (86):

$$\mathrm{ClONO_2} + \mathrm{H_2O} \longrightarrow \mathrm{HOCl} + \mathrm{HNO_3}$$

$$\mathrm{HOCl} + \mathrm{HCl} \longrightarrow \mathrm{Cl_2} + \mathrm{H_2O}$$

*Photochemical Decomposition.* Under laboratory conditions, gaseous HOCl is decomposed by uv light into $Cl_2$, $O_2$, HCl, and $H_2O$ and is initiated by cleavage into HO + Cl radicals. Photolysis of aqueous HOCl is also initiated by formation HO and Cl radicals that undergo a series of further reactions producing hydrochloric and chloric acids and oxygen (87). The half-life of aqueous chlorine ($HOCl/ClO^-$) depends primarily on the wavelength of light and pH. At wavelengths present in sunlight at the earth's surface ($\geq$290 nm), $ClO^-$ absorbs uv light much more strongly than HOCl, thus, the half-life of aqueous chlorine increases with decreasing pH due to the increasing $HOCl/ClO^-$ ratio (88). At ppm concentrations at the surface of the water, values of $t_{0.5}$ calculated from first-order rate constants are 12, 37, and 57 min at pH 8, 7, and 6, respectively. Organic matter in water can consume HO and Cl radicals formed by HOCl photolysis, eg, ethanol gave acetaldehyde and acetic acid, whereas, *n*-butanol and benzoic acid yielded numerous chlorinated products (89).

*Thermal Decomposition.* Dilute, $Cl^-$-free, aqueous hypochlorous acid solutions are quite stable if pure, especially if kept cool and in the dark. For example, at 0°C the initial decomposition rate of a 1 *M* solution is only ~ 0.3% per day (64). At 20°C the decomposition rate is about 10-fold higher ($\Delta E$ ~99.6 kJ $mol^{-1}$). The presence of sodium chloride greatly increases the decomposition rate.

Previous studies showed that the decomposition of HOCl is affected by pH and presence of chloride ion (90). The decomposition exhibits the following overall stoichiometry:

$$2\ \mathrm{HOCl} + \mathrm{ClO^-} \longrightarrow \mathrm{ClO_3^-} + 2\ \mathrm{H^+} + 2\ \mathrm{Cl^-}$$

Chlorine can form at pH $\leq$3: $\mathrm{HOCl} + \mathrm{HCl} \rightleftharpoons \mathrm{Cl_2} + \mathrm{H_2O}$, $K^{25^\circ\mathrm{C}} = 2.54 \times 10^3\ M^{-1}$. The initial step in the current proposed mechanism in the pH range 5–8 is

$$2\ \mathrm{HOCl} \rightleftharpoons \mathrm{Cl_2O \cdot H_2O} \qquad K_\alpha^{50^\circ\mathrm{C}} = 0.030\ M^{-1}$$

where $Cl_2O \cdot H_2O$ is a partially solvated molecule. The rate-controlling step is the oxidation of $ClO^-$ to ${ClO_2}^-$, which occurs via the proposed transient intermediate ${HCl_2O_2}^-$, and is followed by the rapid oxidation of ${ClO_2}^-$ to ${ClO_3}^-$ via the proposed transient intermediate ${HCl_2O_3}^-$ (91):

$$ClO^- + ClO \cdot H_2O \longrightarrow ClO_2^- + HOCl + H^+ + Cl^- \qquad k_1^{50°C} = 3.0\ M^{-1}\ s^{-1}$$

$$ClO_2^- + Cl_2O \cdot H_2O \longrightarrow ClO_3^- + HOCl + H^+ + Cl^- \qquad k_2^{50°C} \geq 6 \times 10^4\ M^{-1}\ s^{-1}$$

A parallel pathway involving HOCl instead of $ClO^-$ is ~1000 times slower: $k_1^{50°C} = 0.0036\ M^{-1}\ s^{-1}$. The formation of chlorate is a third-order process with a maximum decomposition rate at pH 6.9 that is described mathematically by the following differential equation: $d({ClO_3}^-)/dt = K_\alpha k_1[HOCl]^2[ClO^-]$.

*Inorganic Reactions.* Hypochlorous acid oxidizes numerous inorganic substrates.

*Kinetic Studies.* Since HOCl and $ClO^-$ coexist in equilibrium over a wide pH range, kinetic studies are necessary to establish their respective roles (92). The oxidation of ions such as $I^-$, $Br^-$, ${NO_2}^-$, and $SO_3^{2-}$ by aqueous chlorine occurs by $Cl^+$ transfer and can involve general acid catalysis (93). The mechanism involves nucleophilic attack at chlorine rather than at oxygen giving a chloro derivative of the substrate that hydrolyzes to the final product, eg, $HOCl + SO_3^{2-} \rightarrow ClSO_3^- + HO^-$, $ClSO_3^- + H_2O \rightarrow SO_4^{2-} + Cl^- + H^+$. Hypochlorous acid is generally a more reactive oxidant, eg, HOCl oxidizes $Br^-$ ~$2 \times 10^6$ faster than $ClO^-$. Rate constants for $Cl^+$ transfer from HOCl to nucleophiles span 10 orders of magnitude with $SO_3^{2-} > I^- >> Br^- >> Cl^-$ according to anion nucleophilicity (94).

Kinetic studies show that reaction of HOCl with ${ClO_2}^-$ in the 6.6–10.0 pH range proceeds via the proposed intermediate $Cl_2O_2$, which reacts with HOCl forming ${ClO_3}^-$ (95). The reaction of excess HOCl with ${BrO_2}^-$ at p[$H^+$] 6–7 and 25°C proceeds through several pathways: $2\ HOCl + {BrO_2}^- \rightarrow {ClO_3}^- + HOBr + H^+ + Cl^-$ 85%; $HOCl + {BrO_2}^- \rightarrow {BrO_3}^- + H^+ + Cl^-$ 8%; and $3\,HOCl + 2\,BrO_2^- \rightarrow ClO_2 + HOBr + HO^- + Cl^-$ 7% (96). Equilibrium concentrations of $Cl_2O$ and $Cl_2$ (when $Cl^-$ concentration is large) also participate; second-order rate constants are as follows: $k(HOCl) = 1.6 \times 10^2$, $k(Cl_2O) = 1.8 \times 10^5$, and $k(Cl_2) = 8.7 \times 10^5\ M^{-1}\ s^{-1}$. A reaction mechanism has been proposed involving steady state species such as: $HOClOBrO^-$, $HOBrOClO^-$, and $ClOClOBrO^-$.

*Other Reactions.* Hypochlorous acid has important uses in synthesis. For example, concentrated $Cl^-$-free HOCl can be oxidized electrochemically to chloric and perchloric acids (97). Hypochlorous acid, preformed or formed *in situ*, is an intermediate in formation of hypochlorites. Organic solutions of HOCl have been used to prepare $Ca(OCl)_2$, by reaction with CaO or $Ca(OH)_2$, and hydrazine by reaction with $NH_3$ (71).

Available chlorine as HOCl in waste streams can be destroyed by reaction with hydrogen peroxide, which occurs via the postulated intermediate formation of peroxyhypochlorous acid (98): $HOCl + H_2O_2 \rightarrow H_2O + [HOOCl] \rightarrow H_2O + HCl + O_2$. The kinetics of formation and hydrolysis of mono-, di-, and trichloramine formed from HOCl and ammonia have been measured (99). Hypochlorous acid derived from chlorine or hypochlorite is used in water treatment to oxidize ammonia via break-point chlorination ($2\ NH_3 + 3\ HOCl \rightarrow N_2 + 3\ HCl + 3\ H_2O$), which is based on formation of unstable dichloramine and is most rapid at a pH of $\sim 7.5$ (99):

$$2\ NH_3 + 2\ HOCl \longrightarrow 2\ NH_2Cl + 2\ H_2O$$

$$2\ NH_2Cl + 2\ HOCl \longrightarrow 2\ NHCl_2 + 2\ H_2O$$

$$2\ NHCl_2 + H_2O \longrightarrow N_2 + HOCl + 3\ HCl$$

*Organic Reactions.* Hypochlorous acid undergoes a variety of reactions with organic substances including oxidation, addition, *C*- and *N*-chlorination, and ester formation. In many of its reactions, HOCl is generated *in situ* via chlorine hydrolysis: $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$ or by chlorination of base: $NaOH + Cl_2 \rightarrow HOCl + NaCl$.

*Oxidation.* Hypochlorous acid oxidizes many organic ions such as formate, oxalate, cyanide, cyanate, etc and is often involved in oxidation of unwanted or potentially toxic substances. For example, the oxidation of $CN^-$ by chlorine is important in wastewater treatment and proceeds via the intermediate ClCN forming $CNO^-$, which is further oxidized by HOCl primarily to $N_2$ and $CO_2$ (92,94,100). Secondary alcohols are oxidized at room temperature to ketones in high yields by HOCl generated *in situ* from aqueous NaOCl and acetic acid (101,102). Selective oxidation in the presence of a primary alcohol is possible, eg, in methanol, aldehydes are oxidized to methyl esters (102).

*Addition.* The industrial scale reaction of propylene with aqueous chlorine forms primarily the α-propylene chlorohydrin isomer.

$$CH_3CH{=}CH_2 + HOCl \longrightarrow CH_3CHClCH_2OH$$

Dichlorides and ethers are the main by-products in this reaction. Treatment with base produces propylene oxide. Specialty epoxides, eg, butylene oxide, are also produced on an industrial scale by means of HOCl generated from calcium hypochlorite and acetic acid followed by dehydrohalogenation with base. Organic solutions of HOCl in polar solvents such as methylethyl ketone have been used to prepare chlorohydrins (enroute to epoxides) by reaction with olefins (71), Addition of HOCl to vinyl chloride yields chloroacetaldehyde (103); addition to acetylenic compounds produces dichloroketones: $RC{\equiv}CH + 2HOCl \rightarrow RC(O)CHCl_2 + H_2O$ (104). (see ACETYLENE-DERIVED CHEMICALS). Hypochlorous acid adds to oximes of cyclic ketones forming intermediate α-chloronitroso compounds that can be converted to nitro compounds (105).

*C-Chlorination.* Reaction of HOCl, formed from calcium hypochlorite and $CO_2$, with highly substituted alkenes in $CH_2Cl_2$ is a convenient route to allylic chlorides (106). Ketones are chlorinated to α-chloroketones by reaction with HOCl. Acetone initially gives $CH_3COCH_2Cl$ (107). Methyl ethyl ketone gives 78% $CH_3CHClCOCH_3$, 15% $CH_3CH_2COCH_2Cl$, and 7% dichlorides (108). The kinetics of chlorination and subsequent degredation to chloroform of substituted phenols by HOCl have been studied (109).

*N-Chlorination.* Chlorination of amino acids forms unstable *N*-chloro compounds (110). By contrast, stable *N*-chloro compounds are formed by reaction of hypochlorous acid and appropriate N-H compounds, eg, succinimide, sulfonamides, hydantoins, cyanuric acid, melamine, etc. For example, HOCl, formed *in situ* via chlorine hydrolysis, converts di- or trisodium cyanurates to dichloro- and trichloroisocyanuric acids, respectively (111). Chloroisocyanurates can also be prepared from isocyanuric acid or monosodium cyanurate and preformed HOCl (112–114). Hydrolysis of chloroisocyanurates provide HOCl for use in swimming pool disinfection and in bleaching applications. Chlorination of melamine by HOCl forms trichloromelamine which can be chlorinated further to hexachloromelamine.

*Isocyanate Formation.* Isocyanates are prepared via *N*-chlorination of amides with HOCl followed by phase-transfer catalyzed Hoffman rearrangement (115).

*HOCl Carriers.* Insoluble resins that slowly release HOCl in water can be prepared by reaction of HOCl with appropriate N-H containing polymers, eg, exposure of a polyamide resin to 1 *M* HOCl for 24 h at 25°C gave a product with 47% av $Cl_2$ (116).

*Ester Formation.* Under the proper conditions, alcohols can be esterified with HOCl forming isolable alkyl hypochlorites: $ROH + HOCl \rightarrow ROCl + H_2O$.

**3.3. Preparation (Laboratory Scale).** *Chorination of Atomized NaOH.* Reaction of atomized 50% NaOH with gaseous chlorine in a glass reactor at ~110–120°C and condensation of the gases, containing $Cl_2$, $Cl_2O$, and HOCl, produces chloride-free HOCl in concentrations of 35–60% (117,118).

*Surface Chlorination of NaOH.* Chloride-free HOCl solutions of up to 15% and higher can be produced by passing chlorine gas over the surface of a stirred 50–60% NaOH solution at ~5° and scrubbing the off-gases, containing $Cl_2$, $Cl_2O$, and HOCl, in cold water (53).

*From Pure $Cl_2O$.* Chloride-free aqueous solutions of up to 76% HOCl can be obtained by dissolving liquid $Cl_2O$, prepared by reaction of $Cl_2$ with HgO, in the appropriate amount of water (2). Alternatively, the gaseous $Cl_2O$ can be absorbed in cold water to give lower concentrations of HOCl. In addition, a $Cl_2O$ solution in $CCl_4$ can be extracted with $H_2O$ to give $Cl^-$ and $Cl_2$-free HOCl solutions of up to 5 *M* (51).

*Distillation of Aqueous HOCl.* Reduced pressure distillation of a mixture of chlorine octahydrate and HgO provides a distillate with ~25% HOCl (5). Chloride-contaning solutions prepared by rapid chlorination of NaOH or $Ca(OH)_2$ can be flash distilled under vacuum giving $Cl^-$-free HOCl solutions (64). Dilute (1–3%), chloride-containing solutions of HOCl, hypochlorite, or aqueous base, can be stripped in a column against a current of $Cl_2$, steam, and air at 95–100°C and the vapors condensed giving virtually chloride-free HOCl solutions of higher concentration in yields as high as 90% (119,120). Dilute $Cl^-$-free HOCl solutions can be distilled to obtain solutions of higher concentration.

*Chlorination of Aqueous Bi and Hg Oxides.* Chlorination of bismuth or mercuric oxides slurried in water results in precipitation of relatively insoluble basic chlorides, ie, BiOCl and $HgO \cdot HgCl_2$. However, the reaction with $Bi_2O_3$ is slow and does not produce high concentrations of HOCl (121) and with HgO, the HOCl solutions will contain small amounts of mercuric chloride.

*Electrodialysis.* Preparation of aqueous HOCl substantially free of $Cl^-$ from either aqueous $Cl_2$ or HOCl salt solutions has been accomplished by electrodialysis (qv) using semipermeable membranes (122). This method has limited potential because of the unavailability of stable anionic membranes.

*Chloride-Containing.* Chloride-containing solutions of HOCl are readily prepared by reaction of $Cl_2$ with aqueous base and can involve rapid hydrolysis (123) or direct reaction with $HO^-$ (124). Hydrolysis produces equimolar amounts of HOCl and HCl, $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$, $K_{eq}^{25°C} = 3.94 \times 10^{-4}\,M$. A saturated solution of $Cl_2$ (0.091 *M*) at 101 kPa (1 atm) and 25°C is ~6% hydrolyzed to HOCl. Neutralization of the HCl with base allows further chlorine hydrolysis and an increase in the HOCl concentration. When $Cl_2$ is added to strong bases such as NaOH or $Ca(OH)_2$, the reaction occurs stepwise.

$$Cl_2 + 2\ HO^- \longrightarrow ClO^- + Cl^- + H_2O \xrightarrow{Cl_2} 2\ HOCl + 2\ Cl^-$$

Although $Cl^-$ increases the decomposition rate of HOCl, the solutions can be utilized for synthetic and manufacturing purposes, especially if used promptly, kept cold, and relatively diluted.

*Organic Soluions.* Chloride-free organic solutions of HOCl can be prepared in near quantitative yield (98–99%) by extraction of Cl-containing aqueous solutions of HOCl with polar solvents such as ketones, nitriles, and esters (71).

**3.4. Preparation (Industrial Scale).** Various methods for preparing aqueous $Cl^-$-free HOCl solution are available.

*Chorination of Atomized NaOH.* High concentrations of virtually chloride-free solutions of HOCl are obtained by reaction of atomized 50% caustic with excess gaseous chlorine at temperatures above the dew point of the system. The reactor gases, containing $Cl_2$, $Cl_2O$, HOCl, and $H_2O$ are condensed to provide HOCl solutions of up to 60% concentration in high yield. The noncondensed gases (primarily $Cl_2$) are recycled to the reactor. The free-flowing solid NaCl by-product, containing small amounts of chlorate, is recycled to a chloralkali cell (117–118).

*Chlorination of NaOH.* HOCl solutions (8–10%) are prepared in ~99% yield by chlorination of dilute NaOH solutions in a packed column under flow conditions (~0.75-min residence time) at 3–5°C for use in preparation of trichloroisocyanuric acid (113).

*Chlorination of Soda Ash.* A former commercial process for producing aqueous HOCl, was based on the reaction of chlorine and water vapor with sodium carbonate in either a tower or a rotating tubular reactor (56). The resulting gas stream containing $Cl_2$, $Cl_2O$, HOCl, and $CO_2$ was scrubbed in cold water to give 10–15% HOCl solutions containing some chloride. In an improved process, dilute solutions of HOCl are prepared by reaction of an equilibrated mixture of chlorine gas and steam with a metal carbonate in a fluidized bed and scrubbing the gases with water in an absorber (57,125).

**3.5. Analysis.** *Iodometry.* The analysis of HOCl is usually carried out iodometrially using acidic KI as described under $Cl_2O$. The liberated iodine is titrated with thiosulfate and the excess acid with base. The acid consumed is a measure of the HOCl present. Any chlorine present liberates iodine without consumption of acid. Chlorate does not interfere.

$$HOCl + 2\ I^- + H^+ \longrightarrow I_2 + Cl^- + H_2O$$

*Instrumental.* Hypochlorous acid can be distinguished from other chlorine species by amperometry using a membrane electrode (126). Spectrophotometry can also be used to measure HOCl via its absorbance maximum at 235 nm (69). Gaseous mixtures of $Cl_2$, $Cl_2O$, and HOCl can be analyzed by mass spectrometry (62,127).

**3.6. Uses.** Hypochlorous acid, preformed or generated *in situ* from chlorine and water, is an intermediate in the manufacture of chlorohydrins (qv) from olefins (en route to epoxides). It is also used in the production of hypochlorites and chloroisocyanurates from cyanuric acid. (see CYANURIC AND ISOCYANURIC ACIDS) HOCl is used in water treatment for disnifection and oxidation of contaminants such as ammonia. It is the active species that kills bacteria and other microorganisms in municipal water treatment or in swimming pool sanitation when $Cl_2$, hypochlorites, or chloroisocyanurates are used (see WATER; BLEACHING AGENTS). Hypochlorous acid can be used for oxidation of waste streams containing formaldehyde (128).

## 4. Metal Hypochlorites

Hypochlorites, either as solutions or solids, are much more stable than hypochlorous acid. Sodium hypochlorite solution is the principal liquid hypochlorite sold commercially and finds wide use in bleaching and sanitizing applications. One of the novel uses of hypochlorites was for disinfection of Apollo Eleven on its return from the moon (129).

The only known stable solid neutral hypochlorites are those of lithium [13840-33-0], calcium [7778-54-3], strontium [14674-76-1], and barium [13477-10-6]. Calcium also forms two stable basic hypochlorites (calcium hydroxide hypochlorites): $Ca(OCl)_2 \cdot 0.5Ca(OH)_2$ [62974-42-9] and $Ca(OCl)_2 \cdot 2Ca(OH)_2$ [12394-14-8]. Sodium hypochlorite [7681-52-9] does not have good stability and is potentially explosive. Potassium hypochlorite [7778-66-7] exists only in solution. Attempts to isolate the solid have resulted in decomposition (130). Neutral magnesium hypochlorite [10233-03-1] has not been isolated (131), but two stable basic hypochlorites have been prepared. Impure silver (31) and basic zinc hypochlorite (132) compositions have been prepared.

**4.1. Properties.** *Solubility.* The solubilities of Li, Na, and Ca hypochlorites in $H_2O$ at 25°C are 40, 45, and 21%, respectively. Solubility isotherms in water at 10°C have been determined for the following systems: $Ca(OCl)_2$-$CaCl_2$, NaOCl-NaCl, and $Ca(OCl)_2$-NaOCl (133).

*Solution Density.* The densities of approximately equimolar solutions of NaOCl and NaCl are given in several product bulletins (134).

*Thermodynamic Data.* Heats of formation of alkali and alkaline earth hypochlorites are given in reference (7). Thermodynamic properties of hypochlorite ion are: $\Delta H_f^\circ$ $-107.1$ kJ mol$^{-1}$; $\Delta G_f^\circ$ $-36.8$ kJ mol$^{-1}$; and $S^\circ$ 41.8 J K$^{-1}$ mol$^{-1}$

(7). The reduction potential of $ClO^-$ is $ClO^- + H_2O + 2\ e^- \rightarrow Cl^- + 2\ HO^-$, $E^\circ = 0.89$ V (7).

*Spectral Data.* The uv absorption spectrum of $ClO^-$ shows a maximum at 292 nm with absorptivity of 368 $M^{-1}$ cm$^{-1}$ (69).

**4.2. Solution Chemistry.** *Photochemical Decomposition.* The ultimate products of the photolysis of alkaline sodium hypochlorite by uv radiation are chlorate and chloride ions and oxygen (135). The primary processes: $ClO + h\nu \rightarrow Cl^- + O(^3P)$, $ClO + h\nu \rightarrow Cl^- + O(^1D)$, and $ClO^- + h\nu \rightarrow Cl + O^-$ generate transient radicals that react further producing the observed products: $Cl^-$, $ClO_2{}^-$, $ClO_3{}^-$, and $O_2$. The quantum yield ($\phi$) and product selectivity vary with the wavelength of the radiation. The $\phi$ for the three primary reactions vary as follows: 254 nm: 0.074:0.278:0.133, 313 nm: 0.075:0.127:0.02, 365 nm: 0.28:0.08:0. Product selectivities (based on oxygen) at 254 nm are $O_2$ 47% and $ClO_3{}^-$ 53%. Chlorite is observed among the products at 365 nm but not at 254 and 313 nm.

*Thermal Decomposition.* Although hypochlorite solutions are much more stable than HOCl, they are subject to decomposition, which is influenced by concentration, ionic strength, pH, temperature, and impurities. Decomposition of sodium hypochlorite produces oxygen and chloride and chlorate ions as follows:.

$$2\ ClO^- \longrightarrow 2\ Cl^- + O_2$$

$$2\ ClO^- \longrightarrow Cl^- + ClO_2^- \qquad k_1 = 2.1 \times 10^{12} e^{-103{,}800/RT} M^{-1} s^{-1}$$

$$ClO^- + ClO_2^- \longrightarrow Cl^- + ClO_3^- \qquad k_2 = 3.2 \times 10^{11} e^{-87{,}000/RT} M^{-1} s^{-1}$$

where: $k_1$ and $k_2$ are second-order rate constants, $T$ is in kelvin, and the gas constant $R = 8.314$ J K$^{-1}$ mol$^{-1}$. The rate-controlling step to chlorate is the bimolecular formation of chlorite, which reacts rapidly with hypochlorite (136). The uncatalyzed decomposition to oxygen is bimolecular with an activation energy of 111.3 kJ mol$^{-1}$. Although it is much slower than chlorate formation, it is susceptible to catalysis by trace metal impurities (137–139). The most powerful catalysts for accelerating the decomposition to oxygen are Co, Ni, and Cu; Fe and Mn are much less effective. Although these metals do not catalyze chlorate formation, iridium apparently does (140).

*Inorganic Reactions.* Hypochlorites yield HOCl when treated with excess $CO_2$ or stoichiometric amounts of mineral acids and are converted to $Cl_2$ when excess HCl is used. Hypochlorite is easily reduced to chloride ion by various reducing agents. It is also reduced by hydrogen peroxide. The oxidation of various inorganic anions by hypochlorite has been studied kinetically (92). Hypochlorite is a strong oxidant capable of oxidizing $MnO_4^{2-}$ to $MnO_4^-$, $IO_3^-$ to $IO_4^-$, and $Fe^{3+}$ to $FeO_4^{2-}$. Oxidation of $Cu^{2+}$ by alkaline $ClO^-$ in the presence of iodate and tellurate forms $Cu^{3+}$ complexes: $[Cu(IO_4OH)_2]^-$ and $\{Cu[TeO_4(OH)_2]_2\}^{5-}$ (141). Hypochlorite ion is oxidized to chlorate by ozone (142). Its reaction with ammonia to form monochloramine is the basis of the manufacture of hydrazine (qv).

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH \xrightarrow{NH_3} N_2H_4 + NaCl + H_2O$$

*Organic Reactions.* Hypochlorite ion acts as a chlorinating and oxidizing agent toward organic compounds and has numerous interesting and useful synthetic applications (143,144).

*Reaction with Aliphatics.* Saturated hydrocarbons can be chlorinated in moderate yields under mild conditions in a biphasic system consisting of alkaline hypochlorite solution and $CH_2Cl_2$ containing Ni(II) bis(salicylidene)ethylenediamine as chlorination catalyst and hexadecyltrimethylammonium bromide as phase-transfer catalyst (145).

Alkenes are epoxidized in good yield by hypochlorite in water–$CH_2Cl_2$ using Mn(III) porphyrins as epoxidation catalysts and triethylbenzylammonium chloride as phase-transfer catalyst (146). Manganese(III) porphyrin bound to colloidal anion exchange particles was a more effective catalyst for epoxidation of styrene by alkaline $ClO^-$ than in aqueous solution (147). Olefins dissolved in methylene chloride are epoxidized at room temperature by aqueous hypochlorite using Ni(II) bis(salicylidene)-ethylenediamine as epoxidation catalyst and tributylbenzyl-ammonium chloride as phase-transfer catalyst (148,149). Unsaturated aldehydes, ketones, and nitriles are epoxidized in one step in high yield via nucleophilic attack by hypochlorite ion (150–153).

Secondary alcohols are oxidized to ketones in good yields under mild conditions in a triphasic system using an inert solvent, solid $Ca(OCl)_2$, and a hypochlorite resin as catalyst (154). Hypochlorite is employed in the preparation of carboxylic acids by the haloform oxidation and amines by the Hoffmann rearrangement. Aliphatic oximes (155) and primary and secondary nitro compounds (156) are converted to geminal chloro nitro alkanes. Symmetrical dialkyl hydrazines and methylenediamine sulfate are oxidized to azo compounds (157) and diaziridine (158), respectively. Acetylenic protons are displaced to give chloroacetylene (159–161).

*Reaction with Aromatics.* Aromatically bound methylene groups in acetyl substituted aromatics are oxidized by NaOCl to carboxylic acids (162). *o*-Nitroanilines are oxidized in good yields by alkaline hypochlorite to benzofurazan oxides. 2,4-Dinitroaniline, on treatment with NaOCl in alkaline methanol, is converted to 5-chloro-4-methoxybenzofurazan-1-oxide via a haloalkoxy substitution reaction (163); the haloalkoxy reaction has been applied to additional heterocycles, eg, 6-nitroanthroxanic acid (164). Hypochlorite readily chlorinates phenols to mono-, di-, and tri-substituted compounds (165). In water treatment chlorophenols are degraded by excess hypochlorite to eliminate off-flavor (166). Hypochlorite converts bromobenzene to chlorobenzene in a biphasic system at pH 7.5–9 using phase-transfer catalysts (167).

*Reaction with Heterocyclics.* Cyclopentadiene and indene are readily chlorinated by hypochlorite to perchlorocyclopentadiene (168) and 1,1,3-trichloroindene (169), respectively.

**4.3. Solid-State Chemistry.** Thermal decomposition of calcium hypochlorite produces $CaCl_2$, $O_2$, and small amounts of $Ca(ClO_3)_2$. By contrast, sodium hypochlorite produces primarily sodium chlorate. Dichlorine monoxide reacts slowly with moist calcium chloride forming calcium hypochlorite and chlorine (170):

$$CaCl_2 + 2\ Cl_2O \longrightarrow Ca(OCl)_2 + 2\ Cl_2$$

Anhydrous hypochlorites are oxidized to chlorates by $Cl_2O$ (171). The rate of chlorate formation decreases in the order $Na > Ba > Sr > Li > Ca$.

$$M(OCl)_n + 2n\ Cl_2O \longrightarrow M(ClO_3)_n + 2n\ Cl_2$$

In the presence of gaseous chlorine, dry hypochlorites decompose in two ways:

$$M(OCl)_n + n\ Cl_2 \longrightarrow MCl_n + n\ Cl_2O$$

$$2\ M(OCl)_n + 2n\ Cl_2 \longrightarrow 2\ MCl_n + 2n\ Cl_2O \xrightarrow{M(OCl)_n} 2\ MCl_n + M(ClO_3)_n + 2n\ Cl_2$$

Strontium, Li, and Ca hypochlorites react primarily by the first path and NaOCl mainly by the second. In the presence of moisture, chlorate formation is the predominate reaction in all cases.

**4.4. Analysis.** *Available Chlorine.* The av $Cl_2$ in a hypochlorite is a measure of the oxidizing capacity expressed in terms of elemental chlorine; one hypochlorite ion is equivalent to one $Cl_2$ molecule. Thus pure $Ca(OCl)_2$ has an av $Cl_2$ of $(2 \times \text{mol wt } Cl_2)100/[\text{mol wt } Ca(OCl)_2]$ or $(2 \times 70.9/143.0) \times 100 = 99.2\%$.

*Iodometry.* The available chlorine (av $Cl_2$) in hypochlorite solutions or solids is determined by reaction with aqueous KI, followed by acidification with either acetic or sulfuric acid and titration of the liberated iodine with standard thiosulfate ($ClO^- + 2I^- + 2\ H^+ \rightarrow Cl^- + I_2 + H_2O$).

**4.5. Preparation of Hypochlorite Solutions.** Hypochlorite solutions are prepared in near quantitative yield by chlorination of NaOH (caustic soda) or a $Ca(OH)_2$ (hydrated lime) slurry.

$$2\ NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$$

$$2\ Ca(OH)_2 + 2\ Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2\ H_2O$$

The concentration of base depends on the application, eg, ~14% NaOH is used to prepare commercial strength 12.5% NaOCl solutions. Chlorination of 50% NaOH and removal of precipitated salt produces a concentrated, low salt solution (32% NaOCl, 6% NaCl), which is used as a process intermediate in $Ca(OCl)_2$ manufacture. Concentrations as high as 45% can be obtained by melting $NaOCl \cdot 5H_2O$ crystals (mp 18°C) recovered by cooling this solution. Dilution to commercial strength NaOCl produces more stable solutions because of lower salt content. Hypochlorite solutions of varying concentrations can also be prepared by reaction of the appropriate base with $Cl^-$-free HOCl solutions or $CCl_4$ solutions of $Cl_2O$ (31).

**4.6. Preparation of NaOCl–Trisodium Phosphate Complex.** Chlorinated trisodium phosphate [56802-99-4] is a complex with the formula $(Na_3PO_4 \cdot 11H_2O)_4 \cdot NaOCl$ (172). The crystalline, efflorescent product melts at 62°C. It is prepared by crystallization from a liquor containing di- and trisodium phosphate in appropriate ratio containing an excess of 15% NaOCl.

**4.7. Preparation of Solid Lithium Hypochlorite.** High purity lithium hypochlorite can be prepared by reaction of lithium hydroxide with $Cl^-$-free

HOCl (173) or $CCl_4$ solutions of $Cl_2O$ followed by evaporation and drying (31). The monohydrate is free-flowing, nondusty, and of reasonable density. Anhydrous lithium hypochlorite, LiOCl, is a white, lightweight, dusty, hygroscopic, and corrosive powder. When LiOCl is prepared via chlorination of LiOH, sodium hydroxide is used, consequently, the product will contain sodium chloride as a diluent.

### 4.8. Preparation of Basic Calcium Hypochlorites.

Caclium hypochlorite forms two double salts, hemi- and dibasic calcium hypochlorite that have been used as intermediates in preparation of calcium hypochlorite. They form during chlorination of $Ca(OH)_2$ and are formed by reaction of calcium hypochlorite with unreacted $Ca(OH)_2$. Hemibasic calcium hypochlorite is also an item of commerce.

$$Ca(OCl_2)_2 + 0.5\ Ca(OH)_2 \longrightarrow Ca(OCl)_2 \cdot 0.5\ Ca(OH)_2$$

$$Ca(OCl)_2 + 2\ Ca(OH)_2 \longrightarrow Ca(OCl)_2 \cdot 2\ Ca(OH)_2$$

### 4.9. Preparation of Triple Salt.

Chlorination of $Ca(OH)_2$ slurried in strong NaOCl solution, followed by cooling to −15°C, precipitates ~80% of the av $Cl_2$ as large hexagonal crystals of a triple salt: $Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O$ [64147-46-2] (174). The recovered triple salt, free of much of the hydrated lime impurities, can be treated with chlorinated lime slurry to produce neutral calcium hypochlorite dihydrate crystals [22464-76-2].

$$\begin{aligned}2\ Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12\ H_2O + Ca(OCl)_2 \\ + CaCl_2 \longrightarrow 4\ Ca(OCl)_2 \cdot 2\ H_2O + 4\ NaCl + 16\ H_2O\end{aligned}$$

### 4.10. Preparation of Solid Calcium Hypochlorite.

The raw materials for preparation of solid calcium hypochlorite are calcium hydroxide, sodium hydroxide, and chlorine. In addition, a number of process intermediates have been employed, including: sodium hypochlorite, triple salt, and hemibasic and dibasic calcium hypochlorite.

*Coventional Processes.* Chlorination of a sufficiently thick hydrated lime slurry forms equimolar amounts of calcium chloride and calcium hypochlorite, which precipitates as the dihydrate:

$$2\ Ca(OH)_2 + 2\ Cl_2 \longrightarrow Ca(OCl)_2 \cdot 2\ H_2O + CaCl_2$$

The presence of the coproduct $CaCl_2$ is undesirable because it prevents formation of large, easy-to-filter crystals of $Ca(OCl)_2 \cdot 2\ H_2O$ and owing to its hygroscopicity, it impedes drying and has an adverse effect on product stability. Industrial processes, therefore, are designed to eliminate or minimize $CaCl_2$ during processing and in the final product (see CALCIUM COMPOUNDS).

Use of NaOH results in formation of the more desireable by-product sodium chloride, which is not hygroscopic and does not have an adverse effect on calcium hypochlorite crystal size or product stability. Since production of a high assay product requires removal of sufficient amounts of chloride by-product, simply adding NaOH directly to the process is not a viable alternative. Instead, use of preformed low salt (6%), concentrated NaOCl (32%) solution prepared by chlorination of 50% NaOH allows removal of significant amounts of chloride as precipitated NaCl. On reaction with calcium chloride, formed by chlorination of $Ca(OH)_2$ slurry, it forms calcium hypochlorite and sodium chloride.

$$2\ NaOCl + 2\ CaCl_2 \longrightarrow Ca(OCl)_2 + 2\ NaCl$$

Use of NaOCl results in formation of slurry of laminar crystals of calcium hypochlorite dihydrate $[Ca(OCl)_2 \cdot 2H_2O]$ dispersed in a $Ca(OCl)_2$-NaCl instead of $Ca(OCl)_2$-$CaCl_2$. Filtration of calcium hypochlorite dihydrate slurry allows removal of additional salt. Since all of the salt is normally in solution, a large part of it is removed via the filtrate. However, the filtrate still contains a significant amount of dissolved calcium hypochlorite, which represents not only a potential yield loss but also a potential pollution load. Most of the hypochlorite value in the filtrate can be recovered by addition of $Ca(OH)_2$, which precipitates dibasic calcium hypochlorite. The coarse dibasic crystals are easily separated from the liquid phase and sent to the hydrated lime chlorination stage where they are chlorinated in the presence of NaOCl.

$$Ca(OCl)_2 \cdot 2\ Ca(OH)_2 + 2\ NaOCl + 2\ Cl_2 \longrightarrow 3\ Ca(OCl)_2 + 2\ NaCl + 2\ H_2O$$

Although the above process chemistry is straightforward and uncomplicated, a large number of process variations have been patented (174–192).

*Crystal Growth Modifiers.* Crystal growth modifiers have been employed in conventional processes to improve filterability and water retention of $Ca(OCl)_2 \cdot 2H_2O$, which typically crystallizes as fine plates. Addition of zinc dust or salts produces larger square- and diamond-shaped, untwinned dihydrate crystals (193). Coarse prismatic crystals are obtained by use of carbohydrates and carboxylic acids and their salts (194).

*Cocrystallization Processes.* A high assay product can still be produced when sodium hydroxide is used instead of preformed sodium hypochlorite in chlorination of hydrated lime. The overall stoichiometry is

$$Ca(OH)_2 + 2\ NaOH + 2\ Cl_2 \longrightarrow Ca(OCl)_2 \cdot 2\ H_2O + 2\ NaCl$$

The cocrystalline slurry can be separated based on size because the larger salt crystals settle more readily than the smaller calcium hypochlorite dihydrate crystals. Filtrates may still be treated with $Ca(OH)_2$ to recover hypochlorite values by precipitation of dibasic calcium hypochlorite. The PPG process (195–198) is discussed under commercial processes. A number of other processes also employ cocrystallization (199–202).

The PPC process (203) forms dibasic crystals from hydrated lime and recovered filtrates. The dibasic crystals are separated from their mother liquor by decantation, slurried in caustic solution and chlorinated to produce a cocrystalline slurry of $Ca(OCl)_2$ and NaCl. The slurry is sent to a flotation cell where the larger salt crystals settle out and the smaller hypochlorite crystals float to the top with the aid of air and flotation agent. The hypochlorite slurry is centrifuged;

the cake going to a dryer and the centrate to the flotation cell. The salt-rich bottoms from the flotation cell are centrifuged and washed with dibasic mother liquor. The centrates are recycled to the dibasic precipitation step.

*HOCl-Based Processes.* The problem of $CaCl_2$ formation is circumvented by use of chloride-free hypochlorous acid.

$$Ca(OH)_2 + 2\ HOCl \longrightarrow Ca(OCl)_2 + 2\ H_2O$$

Concentrated HOCl (50–60%) is prepared by reaction of chlorine with atomized caustic. After reaction of the concentrated HOCl with $Ca(OH)_2$, the resultant $Ca(OCl)_2$ slurry is dried in a spray grainer or fluidized-bed spray dryer to produce hydrated product with av $Cl_2$ as high as 82% (117,118,204–206).

A former commercial process (207,208) employed a 10–15% hypochlorous acid, prepared by reaction moist chlorine with $Na_2CO_3 \cdot H_2O$ in a rotating tubular reactor, to react with $Ca(OH)_2$ slurry to produce a $Ca(OCl)_2$ solution of ~15–20%, which was spray dried, mixed with salt, compacted, granulated, and dried further.

High purity calcium hypochlorite can be prepared on a labororatory scale by evaporating calcium hypochlorite solutions or slurries obtained by reaction of $Ca(OH)_2$ with $Cl^-$-free HOCl or $CCl_4$ solutions of $Cl_2O$ (31).

*$Cl_2O$-Based Routes.* Calcium hypochlorite can also be prepared by reaction of finely powdered $Ca(OH)_2$ (29) [or moist CaO (30)] with $Cl_2O$; chlorate formation is a competing side reaction.

$$Ca(OH)_2 + Cl_2O \longrightarrow Ca(OCl)_2 \cdot H_2O$$

*Solvent-Based Processes.* Two solvent processes for preparation of $Ca(OCl)_2$ have been described. In one, a $CCl_4$ solution of $t$-$C_4H_9OCl$ is allowed to react with a thin hydrated lime slurry and the aqueous phase, a solution of $Ca(OCl)_2$, is evaporated to a product with a purity of >95% (209). In the other, a cold solution of HOCl in methyl ethyl ketone is reacted with either CaO or $Ca(OH)_2$ (71). Following filtration, the residual solvent in the product is removed under vacuum at low temperature.

### 4.11. Preparation of Bleaching Powder.

Bleaching powder [64175-94-6], known since 1798, is made by chlorination of powdered calcium hydroxide $Ca(OH)_2$, which yields $Ca(OCl)_2$ and $CaCl_2$ and significant amounts of unreacted $Ca(OH)_2$ as well as by-product water. The initial products are dibasic calcium hypochlorite $Ca(OCl)_2 \cdot 2Ca(OH)_2$ and basic calcium chloride $CaCl_2 \cdot Ca(OH)_2$; the dibasic salt undergoes further raection with chlorine yielding a product with ~33–35% av $Cl_2$ (210). The following reaction probably represents the overall process:

$$3.5\ Ca(OH)_2 + 2\ Cl_2 \longrightarrow Ca(OCl)_2 \cdot 0.5Ca(OH)_2 + CaCl_2 \cdot Ca(OH)_2 \cdot 2\ H_2O$$

The poor stability of this original product (made by the old Chamber process), due to the presence of $CaCl_2$ and water, was improved by addition of CaO to combine with water: $CaO + H_2O \rightarrow Ca(OH)_2$. Subsequent process improvements eliminated this necessity by more thorough drying. A more stable product is also obtained by mixing bleaching powder with strong NaOCl solution or by chlorination of a a powdered $Ca(OH)_2$-NaOH mixture (211).

**4.12. Preparation of Solid Dibasic Magnesium Hypochlorite.** So-called basic magnesium hypochlorite [64131-05-1], known for >100 years, and once an item of commerce, had an av $Cl_2$ of ~40–45%. Dibasic magnesium hypochlorite [11073-21-5] has a theoretical av $Cl_2$ of ~58% and was first synthesized in 1969 by addition of either a NaOCl or $Ca(OCl)_2$ solution to an excess of aqueous $MgCl_2$ (212). Hypochlorite hydrates or slurries can also be employed as reactants (212). The reaction proceeds as follows:

$$2\ ClO^- + 2\ Cl^- + 2\ H_2O \rightleftharpoons 2\ Cl_2 + 4\ HO^-$$

$$3\ Mg^{2+} + 2\ ClO^- + 4\ HO^- \longrightarrow Mg(OCl)_2 \cdot 2\ Mg(OH)_2$$

Chlorate formation is a competing side reaction, $3\ ClO^- \rightarrow 2\ Cl^- + ClO_3{}^-$, which decreases the yields of dibasic magnesium hypochlorite and of evolved chlorine. The difficult to filter slurries can be dried with little decomposition to a white, powdery solid with av $Cl_2$ in the range of 52–58%, depending on the type and form of the hypochlorite used. The yields of isolated product and recovered chlorine are typically ~40% each, while product solubility loss and chlorate formation amount to ~10% each.

Dibasic magnesium hypochlorite is more thermally stable than neutral or dibasic calcium hypochlorite. In addition, its decomposition, which starts at ~325°C, is endothermic rather than exothermic as in the case of the Ca compounds.

$$Mg(OCl)_2 \cdot 2\ Mg(OH)_2 \longrightarrow 3\ MgO + Cl_2 + 0.5\ O_2 + 2\ H_2O$$

By contrast, decomposition of dibasic calcium hypochlorite begins at ~265°C to give $Ca(OH)_2$, $CaCl_2$, and $O_2$. Dibasic magnesium hypochlorite exhibits a high degree of stability to moisture as shown by the following relative available chlorine losses at 24°C and 80% rh for 60 day: $Mg(OCl)_2 \cdot 2Mg(OH)_2$ 2%, $Ca(OCl)_2 \cdot 2Ca(OH)_2$ 6%, and $Ca(OCl)_2$ 100%.

Dibasic magnesium hypochlorite can be used as a toilet bowl cleaner (213–215), in laundry and textile bleaches (216,217), and in scouring cleansers (218,219).

**4.13. Commercial Hypochlorite Solutions.** *Sodium Hypochlorite (Liquid Bleach).* Commercial strength liquid bleach used by industries, laundries, and in swimming pool sanitation, contains 12–15% av $Cl_2$ and is sold in 3.8- and 7.6-L polyethylene bottles and 23–57-L carboys, 205-L drums, and tank trucks of ~3-kL capacity and greater. Household bleach contains about 5% av $Cl_2$ and is sold in 1–5.7-L polyethylene containers. Shipping is limited within a short radius of the plant because of transportation costs. Liquid bleach for use in chemical pulp or textile bleaching is usually prepared on site at concentrations of 30–40 g/L of av $Cl_2$ (see BLEACHING AGENTS).

*Manufacture.* Sodium hypochlorite solution is prepared by chlorination of NaOH solution (134). Cooling is necessary, primarily for higher concentrations, since excessive temperatures can result in chlorate formation, representing loss of yield, and may contribute to lower product stability. Since chlorate formation is also a function of concentration, the upper limit of 30°C usually employed with ~6% NaOCl is reduced to ~20°C for 10–15% concentrations. The chlorination of caustic is exothermic and liberates 103.1 $\mathrm{kJ\ mol^{-1}}$ when gaseous $Cl_2$ is used. Liquid chlorine feed is preferred since advantage can be taken of its heat of vaporization, 16.5 $\mathrm{kJ\ mol^{-1}}$, to reduce the cooling requirement. Since 50% caustic is normally employed, and diluted to the desired strength, its heat of dilution, 20.3 $\mathrm{kJ\ mol^{-1}}$, is an additional cooling load. The dilution is controlled by conductivity or density. For preparation of dilute NaOCl solutions, cooling of the caustic is sufficient to absorb the heat of reaction, but for higher concentrations cooling of the hypochlorite solution is also necessary. In batch preparation of dilute hypochlorite, ice can be added directly to the caustic to provide the necessary precooling.

Although manual titration is probably still employed in some small-scale operations for determining the extent of chlorination, monitoring of the oxidation potential is not only more convenient but mandatory in continuous operation. The oxidation potential of the solution is dependent on the half cell reaction: $Cl^- + 2\ HO^- \rightarrow ClO^- + H_2O + 2\ e^-$ and its magnitude is given by the equation:

$$E = E^\circ - 0.0296 \log \frac{[ClO^-]}{[HO^-]^2[Cl^-]}$$

where $E^\circ$ (−0.89 V) is the standard electrode potential at 25°C when concentrations are at unit activity. Although the oxidation potential is essentially a function of pH, its measurement is preferred to pH measurement because of its faster response and lower maintenance requirements (220). The oxidation potential is measured with a potentiometer using an oxidation–reduction potential (ORP) cell consisting of a calomel or silver reference electrode and a platinum indicating electrode.

Agitation of the hypochlorite solution is necessary to minimize local overchlorination and also to reduce any time lag in response of the ORP cell. Air has been used in batch operation for this purpose; however, sufficient agitation can be obtained from the turbulence of the $Cl_2$ feed itself or by recirculating through an external loop. Complete absorption of the $Cl_2$ is ensured by maintaining an adequate depth of solution in the chlorinator. In many continuous systems the $Cl_2$ and caustic are allowed to react in a mixing zone, which may be a packed tubular reactor, with the hypochlorite solution going either to a surge tank or to storage.

The conversion of NaOH is usually limited to ~92–94% for ease of control and to avoid overchlorination. A small excess of NaOH is necessary for adequate storage stability. In certain applications, such as textile-bleaching, little or no free caustic alkalinity is desirable. In bleaching of pulp, a pH adjustment may be made to obtain the necessary degree of activity. Prior to bottling, any suspended solids are allowed to settle or they may be removed by filtration (see BLEACHING AGENTS, PULP AND PAPER).

*Electrochemical Production.* High yields of NaOCl are obtained electrolytically by oxidation of $Cl^-$ at dimensionally stable anodes (221). Sodium hypochlorite is prepared using small diaphragmless or membrane cells, with a capacity of 1–150 kg/day of equivalent $Cl_2$, which produce a dilute hypochlorite solution of 1–3 and 5–6 g/L from seawater and brine, respectively (see CHEMICALS FROM BRINE). They are employed in sewage and wastewater treatment and in commercial laundries, large swimming pools, and aboard ships.

*Calcium Hypochlorite (Bleach Liquor).* Bleach liquor is a solution of $Ca(OCl)_2$ and $CaCl_2$ containing some dissolved $Ca(OH)_2$. The av $Cl_2$ can vary but is typically ~33–35 g/L. Although it has some disadvantages, such as scaling and water treatment problems, which are causing a slow shift to sodium hypochlorite, it has considerable use because of lower cost. It is invariably prepared on site and consumed captively primarily for chemical pulp bleaching.

*Manufacture.* The mechanics of the preparation of bleach liquor by chlorination of hydrated lime slurry is only slightly different than that of sodium hypochlorite, and the heat liberated per mol of chlorine is approximately the same. Continuous systems are preferred because of their lower maintenance requirements. On a sufficiently large scale a lime slaker can be justified. In general, good quality slaked lime, $Ca(OH)_2$ is employed to make a thick slurry that is subsequently diluted to the desired concentration by means of a density controller. The hydrated lime slurry is conveyed to a suitable reactor, such as a tower, where it is contacted with chlorine under the control of an ORP cell. The finished bleach liquor can go to a settling tank for sludge separation or be put through a centrifugal cleaner before going to storage.

*Materials of Construction.* Because of the corrosive nature of moist chlorine and hypochlorite solutions, chemically resistant materials are necessary to prevent metallic contamination of the products and to ensure proper functioning of equipment. Chlorination vessels and reactors can be constructed from fiber glass-reinforced polyester (FRP) or carbon steel with a suitable resistant coating or liner made of rubber, Saran, poly(vinyl Chloride) (PVC), or poly(vinylidene fluoride) (Kynar) (see VINYL POLYMERS; VINYLIDENE POLYMERS). Although dry chlorine can be conveyed in carbon steel, moist chlorine and hypochlorite solutions require the use of solid plastic pipe or plastic-lined steel pipe. Chlorination coils or sparge tubes have been fabricated from silver, lead, glass, or PVC. However, all of these have drawbacks such as high cost, fragility, or deterioration and have been largely supplanted by solid Kynar pipe. Valves with corrosion-resistant fittings such as Teflon-lined ball valves or Kynar-lined diaphragm valves are widely employed. Hypochlorite solutions are pumped by centrifugal pumps with resistant linings such as polypropylene. Heat exchangers, cooling coils, and other equipment such as centrifuges are typically made of titanium.

*Economic Aspects.* U.S. demand (excluding captive consumption) for sodium hypochlorite in 2002 amounted to 261 kt of equivalent chlorine and consisted of 58% industrial strength (1,052 ML of 12.5% NaOCl) and 42% household strength (2,044 ML of 5.25% NaOCl) (222). Growth through 2006 is estimated to be 1.3%/year. Growth in chemical pulp bleaching has declined because of environmental factors and performance disadvantages compared to alternative bleaching agents. Water treatment is the largest and fastest growing sector (~3% annually) and is favored over chlorine where safety is a concern, ie, potable water, wastewater, and cooling water treatment.

U.S. consumption of calcium hypochlorite bleach liquor in 1988 amounted to over 2000 t/year of equivalent $Cl_2$, ~53 ML of liquor containing 3–3.5% av $Cl_2$. No current data are available.

*Uses.* Household bleach (5.25% NaOCl): residential laundry bleach and sanitizer, 80%; institutional and restaurant sanitizer, 18%; residential pool and spa sanitizer 2%. Industrial bleach (12.5% NaOCl): municipal and industrial water treatment (potable water, wastewater, cooling towers, etc), 45%; commercial and municipal swimming pool sanitizer, 33%; commercial laundry bleach, 5%; liquid dishwasher detergents, 5%; textile bleaching, 4%; chemicals (organic synthesis, chlorinated trisodium phosphate, hydrazine, etc), 4%; miscellaneous (food processing, fungicide in oil drilling, sweetening agent in oil refineries, etc.) 4% (222) (see BLEACHING AGENTS).

**4.14. Commercial Solid Hypochlorites.** *Sodium Hypochlorite-Trisodium Phosphate (TSP).* This product can be obtained by crystallization from a liquor having the proper $Na_2O/P_2O_5$ ratio containing an excess of NaOCl.

*Manufacture.* Chlorinated TSP is made batchwise by addition of 15% NaOCl solution to a hot (75–80°C) concentrated liquor consisting of di- and trisodium phosphates, in a mol ratio of ~1:10, in a suitable reactor, eg, a pan mixer (223). The mixture is allowed to cool slowly under constant agitation until crystallization occurs (62°C). When crystallization is complete, cooling is continued to ~45°C and the slightly moist crystals are air dried.

*Av. $Cl_2$.* Although the calculated av $Cl_2$ is 4.66%, commercial material usually contains ~3.65% owing to the presence of salt as well as chlorate from decomposition of NaOCl.

*Stability.* Overdrying can result in decreased stability. The loss in storage is ~0.05% av $Cl_2$ per month.

*Packaging and Shipping.* The product is shipped in 45-kg polyethylene-lined paper bags, 23-kg Fiberpak drums, and 57- and 136-kg Leverpak drums.

*Economic Aspects.* Sodium hypochlorite–TSP complex was commercialized in 1930. Chlorinated TSP is manufactured by Stauffer (a subsidiary of Rhône-Poulenc, Inc.). The consumption, steadily decreasing since 1980, dropped sharply in 1985 because of reduced use in dishwasher detergents. The estimated demand in 1987 was 37,360 t (224).

*Applications.* The principal uses are in scouring cleansers and acid metal cleaners for dairy equipment. Use in dishwasher detergents has been supplanted by chlorinated isocyanurates, which are more cost-effective, more stable in hot water, and possess water softening properties.

*Lithium Hypochlorite.* The commercial product contains a significant amount of diluent by-products such as salt and sodium and potassium sulfates that reduce dustiness, increase bulk density, reduce reactivity, and improve storage stability.

*Manufacture.* A calcined ore containing spodumene [1302-37-0], a crude lithium aluminum silicate, $LiAlSi_2O_6$, is treated with sulfuric acid, neutralized to pH 6, and filtered to remove insolubles. The filtrate containing Li, Na, and K sulfates is treated with NaOH (forming LiOH), cooled to 0°C, and filtered to separate crystallized $Na_2SO_4 \cdot 10H_2O$. Additional NaOH is added followed by chlorination and flash drying of the reaction mixture (225).

*Composition.* Typical product analysis is: LiOCl 30%, NaCl 36%, $Na_2SO_4$ 13%, $K_2SO_4$ 6%, LiCl 4%, $LiClO_3$ 2%, LiOH 1%, $Li_2CO_3$ 2%, and $H_2O$ 7% (226).

*Stability.* The claimed loss of av $Cl_2$ is ∼0.2% per month under normal storage conditions. Decomposition produces almost exclusively chloride and chlorate.

*Packaging and Shipping.* The free-flowing granular product is shipped in polyethylene-lined 45.5 and 181.8-kg fiber drums and 909-kg supersacks. The bulk product is repackaged for retail sales.

*Economic Aspects.* Lithium hypochlorite is produced by Lithium Corporation of America (a subsidiary of FMC) at its plant in Bessemer, North Carolina which has a capacity of about 4000 t/year. Total demand is low owing to higher cost and lower av $Cl_2$ compared to calcium hypochlorite.

*Applications.* Lithium hypochlorite, first introduced in 1964, has limited use in swimming pool and spa sanitation (∼80–90%) and dry laundry bleaches.

*Calcium Hypochlorite.* High assay calcium hypochlorite was first commercialized in the United States in 1928 by Mathieson Alkali Works, Inc. (later part of Olin Corp. and now Arch Chemical Co.) under the trade name HTH (High Test Hypochlorite).

*Producers.* Plant capacities of North American manufacturers of calcium hypochlorite are shown Table 7.

*Manufacture.* Calcium hypochlorite is prepared from chlorine, NaOH, and high purity, completely hydrated lime of high reactivity. The lime should contain low levels of impurities such as silica, MgO, $CaCO_3$, $CaSO_4$, $Al_2O_3$, $Fe_2O_3$, and trace metals such as Co, Ni, Cu, and Mn, since some of these can cause process difficulties and can also affect the quality and stability of the final product.

The process produces a slurry of calcium hypochlorite dihydrate. Slurries containing ∼45% solids can be sprayed into a fluidized bed of granular $Ca(OCl)_2$ (230). The intermediate spray grained granular product containing about 20% water can be dried further by conventional means.

Filter cakes of neutral calcium hypochlorite dihydrate containing 30–50% water (depending on the type of filter) can be dried by various methods, eg, rotary drum, tray drying, spray drying, flash drying, fluidized bed drying, etc. During drying small amounts of $CaCO_3$ form by reaction with $CO_2$ in the air. In addition, some loss of available chlorine occurs forming small amounts of calcium chloride and chlorate. Granulation (preforming) of the product during drying can be accomplished by roll compacting the filter cake mixed with partially dried

Table 7. **Calcium Hypochlorite Producers and Capacities**

| Producer | Plant Location | Capacity, $10^3$ t/year |
|---|---|---|
| Arch Chemical Co.[a] | Charleston, Tenn. | 72.7[b], 10[c] |
| PPG Industries, Inc. | Natrium, W. Va. | 32.7[d] |
| Saskatoon Chemicals, Ltd.[e] | Saskatoon, Sask. | 9.35[f] |

[a] Formerly part of Olin Corp.
[b] 68% product (224).
[c] 78% product (222).
[d] Ref. 224.
[e] Saskatoon's process is based on patents in 227–229. Formerly owned by Weyerhaeuser Canada, it was purchased by Sterling Chemicals Holdings, Inc., Houston, Tex. in 1997.
[f] From Sterling Chemicals press release May 21, 1997.

recycled product into sheets which are then broken up (176,231). The final dried product is screened, the oversize crushed and rescreened, and the undersize roll compacted, granulated and rescreened. The final granular product is free-flowing and essentially dustless. When flash drying is used, the finely powdered product is compacted, granulated, and screened.

*Commercial Processes.* Arch Chemical Co. produces calcium hypochlorite in a plant formerly owned by Olin Corp. The earlier triple salt process (174), originally commercialized in 1928, was modified in 1983 (190–192). In the patented process (192), a slurry of dibasic calcium hypochlorite is mixed with a low salt 32% sodium hypochlorite solution, $Ca(OH)_2$, and hypochlorite liquors and chlorinated. The resultant $Ca(OCl)_2 \cdot 2H_2O$ slurry is filtered, the cake going to the dry-end and the filtrate to the dibasic precipitation step where it reacts with $Ca(OH)_2$. Freshly made granular product typically contains ~71% $Ca(OCl)_2$, ~16% NaCl, ~7% $H_2O$, and small amounts $CaCl_2$, $Ca(ClO_3)_2$, $Ca(OH)_2$, and $CaCO_3$. It is marketed in granular form as a 68% av $Cl_2$ product as well as a 47% av $Cl_2$ inert diluent blended product. The product is also marketed in 65% and 68% av $Cl_2$ tabletted form. Other blended products have also been developed containing: $Na_2S_2O_8$ (232), algicide (233), and anti-scalant (234,235).

Arch also produces a higher assay product in a process that is based on concentrated HOCl (117,118,204–206). Atomized 50% NaOH is reacted with excess gaseous chlorine in a reactor maintained above the dewpoint (>100°C). The reactor gases containing $H_2O$, HOCl, $Cl_2O$, and chlorine pass through a heat exchanger, where the $H_2O$, HOCl, and $Cl_2O$ are condensed forming a concentrated (~50%) HOCl solution. The chlorine is recycled. The HOCl solution is reacted with hydrated lime forming a slurry of $Ca(OCl)_2 \cdot H_2O$, which is spray dried. The freshly made free flowing granular product contains 80–81% av $Cl_2$. It is marketted as a 78% av $Cl_2$ granular product.

PPG formerly operated an HOCl-based process (207,208) that was originally commercialized in 1937. Since 1984 it has operated a cocrystallization process (195–198). According to a PPG patent (195), hydrated lime is slurried with dilute $Ca(OCl)_2$ mother liquor and precipitated as dibasic $Ca(OCl)_2$ by reaction with a stronger hypochlorite filtrate. After thickening in a settling tank, the dibasic slurry is mixed with 50% NaOH and a stronger hypochlorite filtrate and chlorinated to produce a slurry of $Ca(OCl)_2$ dihydrate and NaCl crystals which are classified by elutriation. The salt-rich underflow is centrifuged and the centrate used as the elutriant. The salt is reslurried in dibasic mother liquor and centrifuged to produce a salt cake; the centrate is sent to the dibasic precipitation step. The $Ca(OCl)_2$ rich overflow from the classifier is pressure filtered; the filtrate goes to the dibasic precipitation step and the filter cake to a dryer. The product is marketted in granular and tabletted form with 68 and 73% av $Cl_2$.

*Thermal Analysis.* Heating calcium hypochlorite in a stream of $N_2$ during dta results in dehydration at 65–70°C; further heating causes exothermic decomposition at 200–210°C forming $CaCl_2$, $O_2$, and small amounts of $Ca(ClO_3)_2$.

*Stability.* The stability of neutral calcium hypochlorite is primarily a function of temperature and the concentrations of moisture and hydrated lime impurities. Product containing ~7% water may lose 2–3% av $Cl_2$ during the first year when stored in warehouses without temperature control in moderate climates. Decomposition produces $CaCl_2$, $Ca(ClO_3)_2$, and $O_2$.

Table 8. **Calcium Hypochlorite Statistics[a] $10^3$t**

| Year | Demand[b] | Imports | Exports |
|---|---|---|---|
| 1998 | 70 | 29 | 24 |
| 1999 | 73 | 9 | 26 |
| 2002 | 78 | 9[c] | 34[c] |
| 2003 | 79[d] | 6[c] | 30[c] |

[a] Metric tons of 65–70% calcium hypochlorite (222).
[b] Demand = production + imports − exports.
[c] U.S. Commerce Dept. Data.
[d] Estimated.

*Packaging and Shipping.* Calcium hypochlorite is packaged in retail sizes ranging from 0.45-kg plastic pouches and bottles to 45-kg plastic drums. Bulk product for repackaging is shipped in large drums or supersacks.

*Economic Aspects.* U.S. $Ca(OCl)_2$ demand statistics are shown in Table 8 (222). In 2002, exports amounted to ~33% of annual United States production, and imports amounted to ~9% of domestic production. Export growth is outpacing domestic demand growth. Calcium hypochlorite is increasingly being used in less developed countries for potable water treatment.

From 1994 to 1999, the U.S. market grew at an average rate of ~ 3% per yr. Consumption is expected to grow at ~2% per year through 2003. The growth is occurring primarily in the swimming pool market due mainly to new construction; growth in the industrial sector is relatively stagnant. Calcium hypochlorite is used mainly (~75%) for swimming pool sanitation. Since the mid 1980s calcium hypochlorite lost market share to chloroisocyanurates in the residential in-ground pool sector, however, this trend has stabilized. The loss to isocyanurates has been offset to a minor extent by gains over liquid bleach and chlorine in public pools.

The main foreign producers are Japan, South Africa, and Canada. South Korea, Brazil, and The People's Republic of China are minor producers. Japan's Nippon Soda Co., Ltd. is the world's third largest producer. Two other Japanese producers are Toyo Soda Co., Ltd., and Nankai Chemical Industry, Ltd.

*Applications.* Calcium hypochlorite is used for disinfection in swimming pools and drinking water supplies. It is also used for treatment of industrial cooling water for slime control of bacterial, algal, and fungal origin, and for disinfection, odor control, and BOD reduction in sewage and wastewater effluents. Calcium hypochlorite is employed as a sanitizer in households, schools, hospitals, and public buildings. It is also used for microbial control in restaurants and other public eating places. Calcium hypochlorite is used for bacterial control, odor control, and general sanitation in dairies, wineries, breweries, canneries, food processing plants, and beverage bottling plants. It is employed as a mildewcide in and around the home, boats, campers, and trailers (see DISINFECTANTS AND ANTISEPTICS; INDUSTRIAL ANTIMICROBIAL AGENTS).

*Safety and Handling.* Calcium hypochlorite is heated to ~90°C during drying and thus is stable at normal temperatures encountered in transportation, storage, and use. It decomposes exothermically when heated to ~175°C, releasing oxygen, which will intensify a fire reaching containers of calcium hypochlorite. It should be stored in a cool, dry, and well-ventilated area. Since calcium hypochlorite can react vigorously and sometimes explosively with certain organic and inorganic materials, they should be kept away from it during shipment, storage, use, or disposal. In the event of decomposition or contamination, the container should not be resealed but should be isolated if possible and flooded with sufficient water to completely dissolve and wash away the contents.

*Hemibasic Calcium Hypochlorite.* This basic hypochlorite [62974-42-9] is produced by chlorination of hydrated lime.

$$2.5\ Ca(OH)_2 + 2\ Cl_2 \longrightarrow Ca(OCl)_2 \cdot 0.5\ Ca(OH)_2 + CaCl_2 + 2\ H_2O$$

The actual product contains a higher lime content because of the presence of some dibasic compound. Because of the simplicity of the manufacturing process it is cheaper than neutral calcium hypochlorite, and because of its higher av $Cl_2$ and better stability, it is a superior alternative to bleaching powder.

*Manufacture.* Chlorination of thick hydrated lime slurry at 40–45°C forms large crystals of hemibasic calcium hypochlorite which are filtered and dried yielding a granular product with a $Ca(OH)_2$ content of 20–25% and an av $Cl_2$ of 60–65%.

*Economic Aspects.* The approximate annual world capacity of hemibasic calcium hypochlorite was 28,000 t in 1988 (224). The principal producers are Japan and China; India, and Italy are minor producers.

*Applications.* Hemibasic calcium hypochlorite has been used primarily in China, India, Japan, and lesser developed countries as an alternative to bleaching powder. It can be used in the textile and paper making industries, industrial sewage treatment, household sanitation, potable water treatment, general sanitation, etc.

*Bleaching Powder.* This material is made by chlorination of powdered calcium hydroxide.

*Manufacture.* In a two-stage process, hydrated lime is chlorinated (236,237) in a jacketed reactor equipped with an agitator at 20–25°C and 5.3–12.0 kPa (40–90 Torr) and then at 50–55°C and 4.0–6.7 kPa (30–50 Torr).

*Composition.* Typical product analysis is: 36.8% $Ca(OCl)_2$, 31.7% $CaCl_2$, 26.2% $Ca(OH)_2$, 3.0% $CaCO_3$, 0.2% $Ca(ClO_3)_2$, and 0.9% $H_2O$

*Economic Aspects.* The production of bleaching powder has been steadily declining. Peak U.S. production was 133,400 metric tons in 1923; it decreased to 23,600 t in 1955 and has not been reported since. Imports, averaging 1160 t during 1980–1987, came from India, Spain, the United Kingdom, Germany, and Canada (224). It is probably also manufactured in some less developed countries by the old Chamber process.

*Applications.* The high insoluble (hydrated lime) content is an undesirable feature of bleaching powder owing to the loss of hypochlorite in the sludge that is formed in aqueous slurries. Bleaching powder can be employed for general sanitation and may also be used to disinfect seawater, reservoirs, and drainage ditches where the volume of insolubles is not important. It can be used as a decontaminating agent for areas sprayed with chemical warfare agents such as mustard gas (see CHEMICALS IN WAR).

### 4.15. Organic and Nonmetal Hypochlorites.

*Alkyl Hypochlorites.* Alkyl hypochlorites, esters of hypochlorous acid, are nonpolar, volatile liquids with irritating odors and are extremely lachrimatory. Physical property data is limited (238–241). Primary and secondary hypochlorites are very unstable but tertiary hypochlorites exhibit good stability. *tert*-Butyl hypochlorite, can be prepared by chlorination of an alkaline solution of the alcohol followed by phase separtion of the oily product:

$$t\text{-}C_4H_9OH + NaOH + Cl_2 \longrightarrow t\text{-}C_4H_9OCl + NaCl + H_2O$$

The chemistry of $t$-$C_4H_9OCl$ has been extensively explored (242,243). *tert*-Butyl hypochlorite has been used for the preparation of allylic chlorides (244), ketosteroids and chlorosteroids (245), sulfoxides (246), epoxides (247) and in *N*-chlorination of amines (248), chlorination of 2-amino-1,4-quinones (249), and conversion of anhydropenicillin to the 6-methoxy derivative (250) and unsaturated hydroperoxides to monocyclic and bicyclic chloroalkyl 1,2-dioxolanes.

*tert*-Butyl hypochlorite has been found useful in upgrading vegetable oils (251), in the preparation of α-substituted acrylic acid esters (252), and esters of isoprene halohydrins (253). Numerous patents describe its use in cross-linking of polymers (qv) (254), in surface treatment of rubber (qv) (255), and in odor control of polymer latexes (256). It can be used in the preparation of propylene oxide (qv) in high yield with little or no by-products (247,257).

*Flouroalkyl Hypochlorites.* Numerous fluorinated and perfluorinated alkyl hypochlorites have been synthesized and characterized, eg, $CF_3OCl$ [22082-78-6], $C_2F_5OCl$ [22675-67-8], $i$-$C_3F_7OCl$ [22675-68-9], and $t$-$C_4F_9OCl$ [22082-78-6]. Fluoroalkyl hypochlorites are extremely susceptible to hydrolysis but are much more thermally stable than the corresponding parent compounds (42) and can be prepared by reaction of ClF with the appropriate carbonyl compound or alcohol. The fluoroalkyl hypochlorites readily react with CO and $SO_2$ to form the corresponding chloroformates and chlorosulfates (258). They add to olefins giving α-chloroethers (259) and form borate esters by reaction with $BCl_3$ (260). Fluoroalkyl hypochlorites are useful as insecticides, initiators for polymerizations, and bleaching and chlorinating agents (261).

*Acyl Hypochlorites.* Although no acyl hypochlorites [$RCO_2Cl$] have been isolated in pure form, they have been characterized in solution and employed as reactants via *in situ* generation from $Cl_2O$ or HOCl and carboxylic acids, or from $Cl_2$ and silver salts of carboxylic acids (40,242). Perfluoroacyl hypochlorites have also been prepared (262). Although they are thermally unstable and explosive, $CF_3CO_2Cl$ and $C_3F_7CO_2Cl$ are easily handled and are well characterized.

*Other Hypochlorites.* Inorganic nonmetal unipositive oxychlorine compounds include $ClONO_2$ (22), $ClOClO_3$ (263), and the hypochlorites derived from monobasic fluorine-containing oxyacids of the group VIA elements S, Se, and Te; eg, $HOSO_2F$ (264), $HOSO_2CF_3$ (265), $HOSF_5$ (265,266), $HOSeF_5$ (267), and $HOTeF_5$ (268). In addition, two members of a new class of unipositive chlorine compounds derived from the hydroperoxides $CF_3OOH$ and $SF_5OOH$ have been prepared (269–272).

## BIBLIOGRAPHY

"Chlorine Monoxide, Hypochlorous Acid, and Hypochlorites" under "Chlorine Oxygen Acids and Salts" in *ECT* 3rd ed., Vol. 5, pp. 580–611, by J. A. Wojtowicz, Olin Corp.; in *ECT* 4th ed., Vol. 5, pp. 932–965, by J. A. Wojtowicz, Olin Corp.; "Chlorine Oxygen Acids and Salts, Dichlorine Monoxide, Hypochlorous Acid, and Hypochlorites," in *ECT* (online), posting date: December 4, 2000, by John A. Wojtowicz, Consultant.

## CITED PUBLICATIONS

1. R. Minkwitz and H. Borrmann, *Z. Krist.* **213**, 237 (1998).
2. C. H. Secoy and G. H. Cady, *J. Am. Chem. Soc.* **62**, 1036 (1940).
3. C. F. Goodeve, *J. Chem. Soc.* 2733 (1930).
4. W. A. Roth, *Z. Phys. Chem.* **A191**, 248 (1942).
5. S. Goldschmidt, *Ber.* **52B**, 753 (1919).
6. W. A. Roth, *Z. Phys. Chem.* **145A**, 289 (1929).
7. J. A. Dean, ed., *Langes Handbook of Chemistry*, 15th ed., McGraw-Hill Book Co., New York, 1999.
8. M. Nakata and co-workers, *J. Mol. Spec.* **86**, 241 (1981).
9. H. D. Knauth, H. Alberti, and H. Clausen, *J. Chem. Soc.* **83**, 1004 (1979).
10. Y. Xu and co-workers, *J. Mol. Spect.* **175**, 68 (1992).
11. J. I. Wallace and C. F. Goodeve, *Trans. Faraday Soc.* **27**, 648 (1931).
12. C. H. Cady and R. E. Brown, *J. Am. Chem. Soc.* **67**, 1614 (1945).
13. G. Pannetier and M. B. Caid. *Bull. Soc. Chim.* 1628 (1961).
14. J. J. Beaver and G. Stieger, *Z. Phys. Chem.* **B12**, 93 (1931).
15. N. N. Semenov, *Phys. Z. Sowjetunion* **1**, 561 (1932); E. A. Moelwyn-Hughes and C. N. Hinshelwood, *Proc. R. Soc. London* **131**, 177 (1931).
16. H. J. Schumacher and R. V. Townend, *Z. Phys. Chem.* **B20**, 375 (1933).
17. W. G. Alcock and G. C. Pimentel, *J. Chem. Phys.* **48**, 2373 (1968).
18. K. Stevens, S. Philip, and J. G. Anderson, *J. Phys. Chem.* **96**(1), 706 (1992).
19. C. J. Schack and co-workers, *Inorg. Chem.* **11**, 2201 (1972).
20. Y. Macheteau and L. Gillardeau, *Bull. Soc. Chim.* 4075 (1967).
21. C. J. Shack and D. Pilipovitch, *Inorg. Chem.* **9**, 387 (1970); F. Weniseh, Ph.D. dissertation, Technische Hochschule, Aachen, Germany, 1961.
22. M. Schmeisser, in S. Y. Tyree, Jr., ed., *Inorganic Synthesis*, Vol. 9, McGraw-Hill Book Co., New York, 1967, p. 127; H. Martin and M. Weise, *Z. Elektrochem.* **63**, 162 (1959).
23. M. Schmeisser and K. Brandle, in H. J. Emeleus and A. G. Sharpe, eds., *Advances in Inorganic and Radiochemistry*, Vol. 5, Academic Press Inc., New York, 1963, p. 50.
24. K. Dehnicke, *Angew. Chem.* **73**, 763 (1961).
25. K. Dehnicke, *Chem. Ber.* **97**, 3358 (1964).
26. K. Dehnicke, *Z. Anorg. Allg. Chem.* **309**, 266 (1961).
27. W. E. McDermott, R. E. Lotz, M. L. Delong, and D. M. Thomas, *U.S. NTIS, AD Rep.*, AD-A036781, (1976).
28. R. Schwarz and H. Striebich, *Z. Anorg. Allg. Chem.* **224**, 29 (1935).
29. U.S. Pat. 4,105,565 (Aug. 8, 1978), J. A. Wojtowicz (to Olin Corp.).
30. U.S. Pat. 2,157,559 (May 9, 1939), I. E. Muskat and G. H. Cady (to Pittsburgh Plate Glass Co.).
31. P. Pierron, *Bull. Soc. Chim.* **3**, 660 (1941).
32. M. W. Beach and D. W. Margerum, *Inorg. Chem.* **29**, 1225 (1990).

33. V. M. Gallak, N. I. Bellinskaya, and T. A. Pavlova, *Zh. Prikl. Khim. Leningrad* **38**, 1225 (1965); *J. Appl. Chem.* **38**, 1212 (1965).
34. L. Phillips and R. Shaw, *Proc. Chem. Soc. (London)* 294 (1962).
35. D. D. Tanner and N. Nychka. *J. Am. Chem. Soc.* **89**, 121 (1967).
36. U.S. Pat. 3,782,176 (Mar. 18, 1975), G. L. Kochanny and T. A. Chamberlain (to The Dow Chemical Company).
37. D. D. Tanner, N. Nychka, and T. Ochai, *Can. J. Chem.* **52**, 2573 (1974).
38. G. C. Israel, J. K. Martin, and F. G. Soper, *J. Chem. Soc.* 1286 (1950); G. C. Israel, *J. Chem. Soc.,* 1286 (1950); E. A. Shilov, G. V. Kupinskaya, and A. A. Yasnikov, *Doklady Akad. Nauk S.S.S.R.* **81**, 435 (1951).
39. S. Kolbe, Ph. D. dissertation, Technische Hochschule, Aachen, Germany, 1960.
40. M. Anbar and D. Ginsburg, *Chem. Rev.* **54**, 925 (1954).
41. U.S. Pat. 4,508,695 (Apr. 2, 1985), H. Osburg.
42. D. E. Gould and co-workers, *J. Am. Chem. Soc.* **91**, 1310 (1969).
43. D. J. Sam, F. D. Marsh, W. B. Farnham, and B. E. Smart, in H. Nozaki, ed., *Current Trends In Organic Synthesis*, Proc. Int. Conf., 4th ed., Pergamon Press, Oxford, U.K., 1983, p. 413; F. D. Marsh, W. B. Farnham, D. J. Sam, and B. E. Smart, *J. Am. Chem. Soc.* **104**, 4680 (1982).
44. E. A. Voudrias and M. Reinhard, *Environ. Sci. Technol.* **22**, 1049, 1056 (1988).
45. M. Fujii, Ph.D. dissertation, McGill University, Montreal, Canada, 1969.
46. C. G. Swain and D. R. Crist, *J. Am. Chem. Soc.* **94**, 3195 (1972).
47. P. C. Thapliyal, K. P. Singh, and K. N. Khanna, *Synth. Comm.* **24**, 1089 (1994).
48. U.S. Pat. 3,993,649 (Nov. 23, 1976), D. L. Sawhill and H. W. Schiessl (to Olin Corp.).
49. U.S. Pat. 3,988,336 (Oct. 26, 1976), J. A. Wojtowicz (to Olin Corp.).
50. U.S. Pat. 4,055,719 (Oct. 25, 1977). J. A. Wojtowicz (to Olin Corp.).
51. G. H. Cady, in T. Moeller, ed., *Inorganic Synthesis*, Vol. 5, McGraw-Hill Book Co., New York, 1957, p. 156.
52. C. J. Schack and C. B. Lindahl, *Inorg. Nucl. Chem. Lett.* **3**, 387 (1967).
53. U.S. Pat. 4,147,761 (Apr. 3, 1979), J. A. Wojtowicz and A. J. Klanica (to Olin Corp.).
54. W. A. Noyes and T. A. Wilson, *J. Am. Chem. Soc.* **44**, 1630 (1922); U.S. Pat. 5,152,915 (Oct. 6, 1992), R. W. Ralston, B. L. Duncan, and R. L. Dotson (to Olin Corp.).
55. A. J. Balard, *Ann. Chim. Phys., Ser. 2* **57**, 225 (1834).
56. U.S. Pats. 2,157,524 and 2,157,525 (May 9, 1939), G. H. Cady (to Pittsburgh Plate Glass Co.).
57. U.S. Pat. 4,190,638 (Feb. 26, 1980), H. H. Hoekje and R. R. May (to PPG Industries, Inc.).
58. Ger. Offen. 2,326,601 (Dec. 12, 1974), Brit. Pat. 1,358,839 (July 3, 1974), and Can. Pat. 952,258 (Aug. 6, 1975), W. A. Mueller (to Pulp and Paper Research Institute of Canada).
59. J. H. Hain and H. A. McGee, Jr., *Ind. Eng. Chem. Prod. Res. Dev.* **23**, 490 (1984).
60. U.S. 5,152,915 (Oct. 6, 1992), R. W. Ralston, B. L. Duncan, and R. L. Dotson (to Olin Corp.).
61. J. W. T. Spinks, *J. Am. Chem. Soc.* **53**, 3015 (1931).
62. C. A. Ennis and J. W. Birks, *J. Phys. Chem.* **89**, 188 (1985).
63. E. A. Mishalanie, C. J. Rutkowski, R. S. Hutte, and J. W. Birks, *J. Phys. Chem.* **90**, 5580 (1986).
64. J. A. Wojtowicz, unpublished data.
65. O. M. Lidwell and J. E. Lovelock, *Med. Res. Counc. Spec. Rep. Ser.* **262**, 68 (1948).
66. USSR Pat. 181,058 (Apr. 15, 1966), V. M. Gallak and N. I. Bellinskaya.
67. H. I. Bolker and N. Liebergott, *Pulp Pap. Mag. Can.* **73**, 7332 (1972); U.S. Pat. 3,619,349 (Nov. 9, 1971), N. Liebergott and H. I. Bolker (to Pulp and Paper Institute of Canada); N. Liebergott and B. Van Lierop, *Pulp Pap. Can.* **87**, 300, 324 (1986).

68. U.S. Pat. 5,200,032 (1963), K. Shinohara (to Sony Corp., Japan).
69. J. C. Morris, *J. Phys. Chem.* **70**, 3798 (1966).
70. B. Neumann and G. Muller, *Z. Anorg. Chem.* **182**, 235 (1929); **185**, 428 (1930).
71. U.S. Pats. 3,578,400 (May 11, 1971), and 3,718,598 (Feb. 27, 1973), J. A. Wojtowicz, M. Lapkin, and M. S. Puar (to Olin Corp.); U.S. Pat. 3,845,145 (Oct. 29, 1974), J. A. Wojtowicz, M. Lapkin, and M. S. Puar (to Olin Corp.); U.S. Pat. 3,578,393 (May 11, 1971), J. A. Wojtowicz, M. Lapkin, and M. S. Puar (to Olin Corp.); S. Pat. 3,976,756 (Aug. 24, 1976), J. A. Wojtowicz (to Olin Corp.); U.S.Pat. 5,146,011 (Sept. 8, 1992), M. Shen and J. A. Wojtowicz (to Olin Corp.).
72. J. Ourisson and M. Kastner, *Bul. Soc. Chim.* **6**, 1307 (1939).
73. H. Imagawa, *J. Electrochem. Soc. Jpn.* **18**, 382 (1950); **19**, 271 (1951).
74. G. Holtzwarth, R. G. Balmer, and L. Soni, *Water Res.* **18**, 1421 (1984).
75. E. R. Blatchley and co-workers, *Water Res.* **26**, 99 (1992).
76. C. H. Secoy and G. H. Cady, *J. Am. Chem. Soc.* **63**, 2504 (1941).
77. F. G. Soper, *J. Chem. Soc.* **125**, 227 (1924).
78. B. M. Israel, *Hydrolysis of Some Organohalogenating Agents*, Ph.D. dissertation, University of Wisconsin, 1962.
79. R. A. Ashby, *J. Mol. Spectrosc.* **40**, 639 (1971); J. S. Wells, R. L. Sams, and W. J. Lafferty, *J. Mol. Spectrosc.* **77**, 349 (1979).
80. A. M. Mirri, P. Scappini, and G. Cazzoli, *J. Mol. Spect.* **38**, 218 (1971).
81. O. Wyss, *Water Sewer Works* **109**, 12, 155 (1962).
82. G. M. Fair, J. C. Morris, and S. L. Chang, *J. New Engl. Water Works Assoc.* **61**, 286 (1947).
83. J. E. O'Brien, Ph.D. dissertation, Harvard University, Cambridge, Mass., 1972.
84. R. Atkinson and co-workers, *J. Phys. Chem. Ref. Data* **29**, 167 (2000).
85. J. L. Cook, C. A. Ennis, T. J. Leck, and J. W. Birks, *J. Chem. Phys.* **74**, 545 (1981).
86. T. F. Hanisco and co-workers, *J. Geophys. Res.* **107**, 8278 (2002).
87. A. J. Allmand, P. W. Cunliffe, and R. E. W. Maddison, *J. Chem. Soc.* 822 (1925); 655 (1927); A. J. Allmand and W. W. Webb, *Z. Phys. Chem.* **131**, 189 (1928); L. Bonnet, *Rev. Gen. Mater. Color.* **39**, 29 (1935); K. W. Young and A. J. Allmand, *Can. J. Res.* **27B**, 381 (1949); M. W. Lister, *Can. J. Chem.* **30**, 879 (1952).
88. L. H. Nowell and J. Hoigne, *Water Res.* **26**, 593, 599 (1992).
89. B. G. Oliver and J. H. Carey, *Environ. Sci. Technol.* **11**, 893 (1977).
90. J. I. Aznarez and J. V. Vinade, *Ann. R. Soc. Esp. Fis. Quim.* **B48**, 653, 673 (1952); **49**, 341 (1953); B. P. Nikolskii, V. G. Krunchak, V. V. Palchevskii, and R. I. Sosnovskii, *Dokl. Akad. Nauk SSSR* **197**, 140 (1971); V. G. Krunchaak, *Zh. Prik. Khim.* **47**, 2112 (1973).
91. L. C. Adam, S. Istvan, and G. Gordon, *Inorg. Chem.* **31**, 3534 (1992).
92. M. W. Lister and P. Rosenblum, *Can. J. Chem.* **41**, 2727, 3013 (1963); M. W. Lister and P. Rosenblum, *Can. J. Chem.* **39**, 1645 (1961); M. Anbar and H. Taube, *J. Am. Chem. Soc.* **80**, 1073 (1958); M. W. Lister, *Can. J. Chem.* **34**, 465, 489 (1956); J. Halperin and H. Taube, *J. Am. Chem. Soc.* **74**, 375 (1952); L. Farkas, M. Lewin, and R. Bloch, *J. Am. Chem. Soc.* **71**, 1988 (1949); R. O. Griffith and A. McKeown, *Trans. Faraday Soc.* **28**, 518 (1932).
93. D. W. Johnson and D. W. Margerum, *Inorg. Chem.* **30**, 4845 (1991).
94. C. M. Gerritsen and D. W. Margerum, *Inorg. Chem.* **29**, 2757 (1990).
95. G. Gordon and S. Tachiyashiki, *Environ. Sci. Technol.* **25**, 468 (1991).
96. J. S. Nicoson and co-workers, *Inorg. Chem.* **42**, 5818 (2003).
97. World Pat. 9,114,614 (Oct. 17, 1991), D. W. Crawford and co-workers (to Olin Corp.).
98. R. E. Connick, *J. Am. Chem. Soc.* **69**, 1509 (1947).
99. E. Gray, Ph. D. dissertation, Purdue University, West Lafayette, Ind., 1977; K. Kumar, R. W. Shinness, and D. W. Margerum, *Inorg. Chem.* **22**, 1449 (1983);

C. T. Jafvert, Ph. D. dissertation, University of Iowa, Iowa City, Iowa, 1985; B. M. Saunier and R. E. Selleck, *J. Am. Water Works Assoc.* **71**, 164 (1979).

100. N. S. Chamberlain and H. B. Snyder, "Technology of Treating Plating Wastes," *Tenth Annual Wastes Conference*, Purdue University, Lafayette, Ind., May 1955.
101. R. V. Stevens, K. T. Chapman, and H. N. Weller, *J. Org. Chem.* **45**, 2030 (1979).
102. R. V. Stevens and co-workers, *Tetrahedron Lett.* **23**, 4647 (1982).
103. U.S. Pat. 2,060,303 (Nov. 10, 1936), H. P. A. Groll and G. Hearne (to Shell Dev. Co.).
104. F. Strauss and co-workers, *Berichte* **63**, 1868 (1930).
105. E. J. Corey and H. Estreicher, *Tetrahedron Lett.* **21**, 1117 (1980).
106. S. G. Hodge and co-workers, *Tetrahedron Lett.* **21**, 441 (1980).
107. V. M. Markownikoff, *Annalin.* **153**, Z54 (1870).
108. J. A. Wojtowicz, *Petroleum Chemistry Section*, 161st ACS Meeting, paper No. 16, Los Angeles, Calif., Apr. 1971.
109. H. Gallard and U. von Gunten, *Environ. Sci. Technol.* **36**, 884 (2002).
110. W. D. Stanbro and W. D. Smith, *Env. Sci. Eng.* **13**, 446 (1979); Z. Alouini and R. Seux, *Water Res.* **21**, 335 (1987).
111. U.S. Pat. 2,964,526 (Dec. 13, 1960), W. L. Robinson (to Monsanto Chemical Co.).
112. U.S. Pat. 3,712,891 (Jan. 23, 1973), S. Berkowitz and R. N. Masiah (to FMC Corp.).
113. U.S. Pat. 3,835,134 (Sept. 10, 1974), H. W. Schiessl, L. Sawhill, and S. K. Bhutani (to Olin Corp.).
114. U.S. Pat. 4,024,140 (May 17, 1977), J. A. Wojtowicz (to Olin Corp.); World Pat. 9,308,177 (Apr. 29, 1993), H. W. Hammond, J. H. Shaffer, J. A. Wojtowicz, L. R. Ward, and J. M. Borcz (to Olin Corp.).
115. U. S. Pat. 5,319,133 (Jun. 7, 1994), R. J. Raynor and T. A. Knowles (to Olin Corp.).
116. U.S. Pat. 5,093,431 (Mar. 3, 1992), R. J. Raynor (to Olin Corp.).
117. U.S. Pat. 4,146,578 (Mar. 27, 1979), J. P. Brennan, J. A. Wojtowicz, and P. H. Campbell (to Olin Corp.).
118. U.S. Pat. 5,037,627 (Aug. 6, 1991), J. K. Melton, J. H. Shaffer, G. E. Hilliard, and J. A. Wojtowicz (to Olin Corp.).
119. U.S. Pat. 1,510,790 (Oct. 7, 1924), K. P. McElroy (to Carbide and Carbon Chemicals Corp.); Brit. Pat. 543,944 (Mar. 20, 1942), C. Carter and E. R. B. Jackson (to Imperial Chemical Industries).
120. U.S. Pat. 2,347,151 (Apr. 18, 1944), C. C. Crawford and T. W. Evans (to Shell Dev. Co.).
121. Fr. Pat. 851,659 (Jan. 12, 1940), J. Ourisson and M. Kastner (to Potasse et Produits Chimiques).
122. U.S. Pat. 3,616,385 (Oct. 26, 1971), R. K. Kloss and G. W. Claybaugh (to Procter & Gamble).
123. R. B. Connick and Y. Chia, *J. Am. Chem. Soc.* **81**, 1280 (1959); M. Eigen and K. Kustin, *J. Am. Chem. Soc.* **84**, 1355 (1962).
124. C. W. Spalding, Ph.D. dissertation, University of Wisconsin, June 1961.
125. U.S. Pats. 4,504,456 (Mar. 12, 1985) and 4,584,178 (Apr. 22, 1986), R. E. Yant and R. J. Galluch (to Quantum Technologies, Inc.).
126. J. D. Johnson, J. W. Edwards, F. J. Keesler, *J. Am. Water Works Assoc.* **70**, 341 (1978).
127. T. E. Caldwell and co-workers, *J. Phys. Chem.* **103**, 8231 (1999).
128. U.S. Pat. 5,244,581 (Feb. 1, 1992), A. P. Murphy (to U.S. Dept. of Interior).
129. H. A. Podoliak, *A Review of The Literature On the Use of Calcium Hypochlorite In Fisheries*, NTIS, U.S. Dept. Commerce, Washington, D.C., Mar. 1974.
130. Gmelins Handbuch der Anorganischen Chemie, 8 Aufl., System Nr. 22, Verlag Chemie, Weinheim, Germany, 1937, p. 471.
131. *Ibid.*, System Nr. 27B, 1939, p. 150.

132. J. A. W. Luck, *J. Am. Pharm. Assoc.* **13**, 710 (1924).
133. S. Z. Makarov and E. F. Shcharkova, *Russ. J. Inorg. Chem.* **14**, 1632 (1969).
134. *A Practical Guide to Chlorine Bleach Making*, Technical and Engineering Service Bulletin 72–19, Allied Chem. Corp., Morristown, N.J., 1974; Soda Bleach Solutions, Diamond Alkali Co., 1952.
135. G. V. Buxton and M. S. Subhani, *J. Chem. Soc. Faraday* **1**, 68, 947, 958, 970 (1972).
136. M. W. Lister, *Can. J. Chem.* **34**, 465 (1956); **40**, 729 (1962).
137. *Ibid.*, **34**, 479; E. Chirnouga, *J. Chem. Soc.* 1693 (1926).
138. O. R. Howell, *Proc. R. Soc London Ser. A* **104**, 134 (1923).
139. J. R. Lewis, *J. Phys. Chem.* **32**, 243, 1808 (1928); **35**, 915 (1931); **37**, 917 (1933).
140. G. H. Ayers and M. H. Booth, *J. Am. Chem. Soc.* **77**, 825 (1955).
141. W. Levason and M. D. Spicer, *Coord. Chem. Rev.* **76**, 45 (1987).
142. J. Hoigne and co-workers, *Water Res.* **19**, 993 (1985).
143. R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry*, John Wiley & Sons, Inc., New York, 1953, pp. 422, 674.
144. L. F. Feaser and M. Feaser, *Reagents for Organic Synthesis*, John Wiley & Sons, Inc., Vols. 1–17.
145. C. Querci, S. Strologo, and M. Ricci, *Tetrahedron Lett.* **45**, 6577 (1990).
146. A. W. van der Made, R. J. M. Nolte, and W. Drenth, *Recueil des Travaux Chimiques des Pays-Bas.* **109**, 537 (1990).
147. H. Turk and W. T. Warren, *J. Org. Chem.* **56**, 1253 (1991).
148. H. Yoon and C. J. Burrows, *J. Am. Chem. Soc.* **110**, 4048 (1988).
149. H. Yoon, T. R. Wagler, K. J. O'Connor, and C. J. Burrows, *J. Am. Chem. Soc.* **112**, 4508 (1990).
150. S. Marmor, *J. Org. Chem.* **28**, 250 (1963).
151. U.S. Pat. 2,887,498 (May 19, 1959), G. W. Hearne, D. S. LaFrance, and H. de V. Finch (to Shell Development Co.).
152. C. Schaer, *Helv. Chim. Acta.* **41**, 560, 614 (1958).
153. D. H. Rosenblatt and G. H. Broome, *J. Org. Chem.* **28**, 1290 (1963).
154. M. Schneider, J. Weber, and P. Faller, *J. Org. Chem.* **47**, 364 (1981).
155. E. M. Cherkasova and co-workers, *Z. Obsc. Khim.* **19**, 321 (1949).
156. F. Asinger, *Chemie Und Technologie Der Paraffin-Kohlenwasserstoffe*, Akademie Verlag, Berlin, Germany, 1956, p. 300.
157. R. Ohme, H. Preuschof, and H. U. Heyne, *Org. Synth.* **52**, 11 (1972).
158. R. Ohme and E. Schmitz, *Berichte* **97**, 297 (1964).
159. F. Strauss and co-workers, *Berichte* **63**, 1873 (1930).
160. R. A. Jacobson and W. H. Carothers, *J. Am. Chem. Soc.* **55**, 4667 (1933).
161. J. Cologne and L. Cumet, *Bull. Soc. Chim.* **14**, 842 (1947).
162. D. D. Neiswender, Jr., W. B. Moniz, and J. R. Dixon, *J. Am. Chem. Soc.* **82**, 2876 (1960).
163. F. B. Mallory, C. S. Wood, and B. M. Hurwitz, *J. Org. Chem.* **29**, 2605 (1964).
164. D. R. Eckroth, T. C. Cochran, and E. C. Taylor, *J. Org. Chem.* **31**, 1303 (1966).
165. B. F. Clark, *Chem. News* **143**, 265 (1931).
166. H. R. Eisenhauer, *J. Water Pollut. Control Fed.* **36**, 1116 (1964).
167. R. G. Landolt and co-workers, *J. Org. Chem.* **57**, 39 (1992).
168. R. Riemschneider, *Chim. Ind.* **34**, 266 (1952).
169. F. Strauss and co-workers, *Berichte* **63**, 1885 (1930).
170. U.S. Pat. 2,225,923 (Dec. 24, 1940), I. E. Muskat and G. H. Cady (to Pittsburgh Plate Glass Co.).
171. P. Pierron, *Bull. Soc. Chim.* **8**, 664 (1941).
172. U.S. Pat. 1,965,304 (July 3, 1934), H. Adler (to Victor Chemical Works).

173. World Pat. 9,113,025 (Sept. 5, 1991), B. L. Duncan, L. D. Carpenter, L. R. Osborne, and W. T. Wooden (to Olin Corp.).
174. U.S. Pat. 1,718,285 (June 25, 1929), A. George (to Mathieson Alkali Works, Inc.); U.S. Pat. 4,335,090 (Mar. 4, 1982), W. J. Sakowski (to Olin Corp.).
175. U.S. Pat. 1,713,650 (May 21, 1929), A. George and R. B. MacMullin (to Mathieson Alkali Works, Inc.).
176. U.S. Pat. 1,787,048 (Dec. 30, 1930), R. B. MacMullin and M. C. Taylor (to Mathieson Alkali Works, Inc.).
177. U.S. Pats. 2,441,337 (May 11, 1948), 2,469,901 (May 10, 1949), and 2,587,071 (Feb. 26, 1952), J. W. Sprauer (to Pennsylvania Salt Corp.).
178. J. Ourisson, *Bull. Soc. Ind. Mulhouse* **103**, 217 (1938).
179. U.S. Pat. 3,895,099 (July 15, 1975), W. J. Sakowski (to Olin Corp.).
180. U.S. Pat. 3,954,948 (May 1, 1976), W. J. Sakowski (to Olin Corp.).
181. J. Ourisson, *Atti Congr. Intern. Chim. 10th Congr. Rome* **4**, 40 (1939).
182. Fr. Pat. 825,903 (Mar. 17, 1938), and Brit. Pat. 187,009 (June 14, 1938), J. Ourisson.
183. Fr. Pats. 858,057 (Nov. 16, 1940), 862,483 (Mar. 7, 1941), J. Ourisson, P. Camescasse, and M. Kastner (to Potasse et Produits Chimiques).
184. Fr. Pat. 1,019,027 (Jan. 15, 1953), A. J. Vorburger (to Potasse et Produits Chimiques).
185. Brit. Pat. 378,847 (Aug. 16, 1932), F. N. Kitchen (to Imperial Chemical Industries, Ltd.).
186. Brit. Pat. 404,627 (Jan. 15, 1934), F. T. Meehan and F. N. Kitchen (to Imperial Chemical Industries, Ltd.).
187. U.S. Pat. 3,094,380 (June 18, 1963), E. A. Bruce (to Pennsalt Chem. Corp.).
188. U.S. Pat. 3,030,177 (Apr. 17, 1962), J. C. Mohan, Jr. (to Pennsalt Chemical Corp.).
189. Jpn. Pat. 010044 (Feb. 3, 1976), M. Kikuchi and T. Murakami (to Toyo Soda Kogyo Co., Ltd.).
190. U.S. Pat. 4,468,377 (Aug. 28, 1984), W. J. Sakowski, M. C. Bajaj, and B. L. Duncan (to Olin Corp.).
191. U.S. Pat. 4,367,209 (Jan. 4, 1983), W. J. Sakowski and B. L. Duncan (to Olin Corp.).
192. U.S. Pat. 4,399,117 (Aug. 16, 1983), W. J. Sakowski (to Olin Corp.); U.S. Pat. 4,487,751 (Dec. 11, 1984), C. A. Foster and J. H. Shaffer (to Olin Corp.).
193. U.S. Pat. 3,440,024 (Apr. 22, 1969), J. P. Faust and H. L. Robson (to Olin Mathieson Chem. Corp.).
194. U.S. Pat. 4,248,848 (Feb. 3, 1981), T. Murakami, M. Kikuchi, and K. Igawa (to Toyo Soda Mfg. Co., Ltd.).
195. U.S. Pat. 4,328,200 (May 4, 1982), C. N. Welch, C. E. Loehr, R. A. Crawford, and J. E. Carbaugh (to PPG Industries, Inc.).
196. U.S. Pat. 4,390,512 (Jan. 28, 1983), C. E. Loehr, R. A. Crawford, J. E. Carbaugh, and C. N. Welch (to PPG Industries, Inc.).
197. U.S. Pat. 4,428,919 (Jan. 31, 1984), D. A. Stermole, C. E. Loehr, and D. S. Chun (to PPG Industries, Inc.).
198. U.S. Pat. 4,448,759 (May 15, 1984), D. S. Chun, D. A. Stermole, and C. E. Loehr (to PPG Industries, Inc.).
199. U.S. Pat. 3,251,647 (May 17, 1966), B. H. Nicolaisen (to Olin Mathieson Chemical Corp.).
200. U.S. Pat. 3,572,989 (Mar. 30, 1971), S. Tatara and co-workers (to Nippon Soda Co., Ltd.).
201. U.S. Pat. 3,767,775 (Oct. 23, 1973), S. Tatara and co-workers (to Nippon Soda Co., Ltd.).
202. U.S. Pat. 3,950,499 (Apr. 13, 1976), N. Miyashin and co-workers (to Nippon Soda Co., Ltd.).

203. U.S. Pat. 4,258,024 (Mar. 24, 1981), J. O. Hoffer, J. C. Guelen, P. J. Portes, and J. P. Haller (to Potasse et Produits Chimiques).
204. U.S. Pat. 4,416,864 (Nov. 22, 1983), J. A. Wojtowicz (to Olin Corp.).
205. World Pat. 9014306 (Nov. 29, 1990), J. H. Shaffer, J. K. Melton, and G. E. Hilliard (to Olin Corp.).
206. World Pat. 9014143 (Nov. 29, 1990), J. H. Shaffer, W. L. Kurtz, and J. H. Hubbard (to Olin Corp.).
207. U.S. Pat. 2,240,344 (Apr. 29, 1941), I. E. Muskat and G. H. Cady (to Pittsburgh Plate Glass Co.).
208. U.S. Pat. 3,134,641 (May 26, 1964), R. D. Gleichert (to Pittsburgh Plate Glass Co.).
209. U.S. Pat. 1,481,040 (Jan. 15, 1924), M. C. Taylor, R. B. MacMullin, and R. E. Gegenheimer (to Mathieson Alkali Works, Inc.); U.S. Pat. 1,623,483, 1,623,485 (June 14, 1927), R. B. MacMullin (to Mathieson Alkali Works, Inc.).
210. C. W. Bunn, L. M. Clark, and I. L. Clifford, *Proc. R. Soc. London Ser. A* **151**, 141 (1935).
211. U.S. Pat. 4,197,284 (Apr. 8, 1980), J. A. Wojtowicz (to Olin Corp.).
212. U.S. Pat. 3,582,265 (June 1, 1971), J. J. Bishop and S. I. Trotz (to Olin Corp.); U.S. Pat. 4,017,605 (Jan. 31, 1978), J. A. Wojtowicz (to Olin Corp.); U.S. Pat. 4,380,533 (Apr. 19, 1983), J. A. Wojtowicz (to Olin Corp.).
213. U.S. Pat. 4,200,606 (Apr. 29, 1980), D. J. Kitko (to Procter & Gamble Co.).
214. U.S. Pat. 4,246,129 (Jan. 20, 1981), M. L. Kacher (to Procter & Gamble Co.).
215. U.S. Pat. 4,253,950 (Mar. 3, 1981), J. A. Wojtowicz (to Olin Corp.).
216. U.S. Pat. 4,236,891 (Dec. 2, 1980), M. Scardera and G. Schifilliti (to Olin Corp.).
217. U.S. Pat. 4,123,377 (Oct. 3, 1978), C. R. Davey and P. J. Buckley (to Procter & Gamble Co.).
218. U.S. Pat. 4,005,027 (Jan. 25, 1977), W. L. Hartman (to Procter & Gamble Co.).
219. U.S. Pat. 4,248,728 (Feb. 3, 1981), R. L. Puryear (to Procter & Gamble Co.).
220. D. J. Pye, *J. Electrochem. Soc.* **97**, 245 (1960).
221. P. M. Robertson, W. Gnehm, and L. Ponto, *J. Appl. Electr.* **13**, 307 (1983).
222. Sodium Hypochlorite Chemical Profile, Chemical Marketing Reporter, Mar. 24, 2003; Calcium Hypochlorite Chemical Profile, Chemical Marketing Reporter, Oct. 31, 2002.
223. R. N. Bell, *Ind. Eng. Chem.* **41**, 2901 (1949).
224. “Hypochlorite Bleaches” *Chemical Economics Handbook*, Stanford Research Institute International, Stanford, Calif, Apr. 1989.
225. Belg. Pat. 628,396 (May 1963), G. J. Orazem, R. B. Ellestad, J. R. Nelli (to Lithium Corp. of America).
226. Lithium Hypochlorite Product Blletin, FMC Corp., Bessemer City, NC.
227. U.S. Pat. 4,364,917 (Dec. 21, 1982), H. H. Tiedemann, G. Thibault, J. G. J. Laberge (to Chemetrics International, Ltd.).
228. U.S. Pat. 4,374,155 (Feb. 15, 1983), H. H. Tiedemann (to Chemetrics International, Ltd.).
229. U.S. Pat. 4,397,832 (Aug. 9, 1983), G. Thibault, D. C. Mayotte (to Chemetrics International, Ltd.).
230. U.S. Pat. 3,969,546 (July 13, 1976), W. C. Saeman (to Olin Corp.).
231. U.S. Pats. 2,195,755 and 2,195,757 (Apr. 2, 1940), H. L. Robson and G. A. Petroe (to Mathieson Alkali Works, Inc.).
232. U.S. Pat. 4,780,216 (Oct. 25, 1988), J. A. Wojtowicz (to Olin Corp.).
233. U.S.Pat. 5,164, 109 (Nov. 17, 1992), J. A. Wojtowicz (to Olin Corp.).
234. U.S. Pat. 5,004,549 (Apr. 2, 1991), R. B. Wood, R. M. Mullins, and J. A. Wojtowicz (to Olin Corp.).

235. U.S. Pat. 5,112,521 (May 12, 1992), R. B. Wood, R. M. Mullins, and J. A. Wojtowicz (to Olin Corp.).
236. Can. Pat. 194,216 (Nov. 25, 1919), A. Rudge.
237. Ger. Pat. 656,413 (Feb. 4, 1938), E. Renschler and A. Remele (to I. G. Farbenindustrie AG).
238. M. Anbar and I. Dostrovsky, *J. Chem. Soc.* 1105 (1954).
239. M. Anbar, Ph.D. dissertation, Hebrew University, Jerusalem, Israel, 1953.
240. M. C. Taylor, R. B. McMullin, and C. A. Gammal, *J. Am. Chem. Soc.* **47**, 395 (1925).
241. J. W. Westwater and L. F. Audrieth, *Ind. Eng. Chem.* **46**, 1281 (1954).
242. E. A. Shilov and G. V. Kupinskaya, *Doklady Akad. Nauk S.S.S.R.* **81**, 621 (1951).
243. M. Anbar and I. Dostrovsky, *J. Chem. Soc.* 1094 (1954).
244. C. Walling and W. Thaler, *J. Am. Chem. Soc.* **83**, 3877 (1961).
245. J. J. Beereboom and co-workers, *J. Am. Chem. Soc.* **75**, 3500 (1953).
246. C. R. Johnson and J. J. Rigau, *J. Am. Chem. Soc.* **91**, 5398 (1969).
247. U.S. Pat. 3,756,976 (Sept. 4, 1973), C. A. Uranek and J. E. Burleigh (to Phillips Petroleum Co.).
248. W. E. Bachmann, M. P. Cava, and A. S. Dreiding, *J. Am. Chem. Soc.* **76**, 5554 (1954).
249. H. W. Moore and G. Cojipe, *Synthesis,* 49 (1973).
250. J. E. Baldwin and co-workers, *J. Am. Chem. Soc.* **95**, 2401 (1973).
251. H. M. Teeter and co-workers, *Ind. Eng. Chem.* **41**, 849 (1949).
252. U.S. Pat. 2,514,672 (July 11, 1950), D. D. Reynolds and W. O. Kenyon (to Eastman Kodak Co.).
253. U.S. Pat. 2,511,870 (June 20, 1950), W. Oroshnik (to Ortho Pharmaceutical Co.).
254. U.S. Pat. 3,960,822 (June 1, 1976), P. Davis, H. C. Vogt, and C. F. Deck (to BASF Wyandotte Corp.).
255. S. Pat. 3,940,548 (Feb. 24, 1976), and Brit. Pat. 1,396,090 (May 29, 1975), Y. Todani and T. Ohkawa (to Nippon Zeon Co., Ltd.).
256. Ger. Offen. 3,016,667 (Nov. 13, 1980), A. P. Gelbein, P. Abraham, and S. Arthur (to C. E. Lummus).
257. Ger. Offen. 2,541,526 (Apr. 1, 1976), A. P. Gelbein and J. T. Kwon (to Lummus Co.).
258. D. E. Young and co-workers, *J. Am. Chem. Soc.* **92**, 2313 (1970).
259. L. R. Anderson and co-workers, *J. Org. Chem.* **35**, 3730 (1970).
260. D. E. Young, L. R. Anderson, and W. B. Fox, *Inorg. Chem.* **10**, 2810 (1971).
261. U.S. Pat. 3,689,563 (Sept. 5, 1972), D. E. Young, L. R. Anderson, and W. B. Fox (to Allied).
262. D. D. DesMarteau, *174th ACS Meeting*, Chicago, Ill., Aug. 1977.
263. C. J. Schack and D. Pilipovich, *J. Am. Chem. Soc.* **92**, 1387 (1970).
264. W. P. Cilbreath and G. H. Cady, *Inorg. Chem.* **2**, 496 (1963).
265. D. D. DesMarteau, *175th ACS Meeting*, Anaheim, Calif., Mar. 1978.
266. C. J. Schack and co-workers, *J. Am. Chem. Soc.* **91**, 2907 (1969).
267. K. Seppelt, *Chem. Ber.* **106**, 1571 (1973).
268. K. Seppelt and D. Nothe, *Inorg. Chem.* **12**, 2727 (1973).
269. F. Aubke and D. D. DesMarteau, in P. Tarrant, ed., *Fluorine Chemistry Reviews*, Vol. 8, Marcel Dekker, Inc., New York, 1977, p. 73.
270. D. D. DesMarteau and R. M. Hammaker, *Isr. J. Chem.* **17**, 103 (1978).
271. N. Walker and D. D. DesMarteau, *J. Am. Chem. Soc.* **97**, 13 (1975).
272. C. T. Ratcliffe and co-workers, *J. Am. Chem. Soc.* **93**, 3886 (1971).

JOHN A. WOJTOWICZ
Olin Corp., Retired