The Chemistry of Chlorine Monoxide (Dichlorine Monoxide)

J. J. RENARD[†] and H. I. BOLKER*

Pulp and Paper Research Institute of Canada, Pointe Claire, Quebec, Canada H9R 3J9

Received December 9, 1974 (Revised Manuscript Received August 27, 1975)

Contents

I. Introduction

In the first reported synthesis of chlorine monoxide (1834), A. J. Balard, a French chemist, prepared a concentrated solution of hypochlorous acid by treating an aqueous chlorine solution with mercuric oxide. Then, upon careful addition of anhydrous calcium nitrate, he observed the evolution of a gas. Its composition was determined by Balard[1,2] and by Gay-Lussac,[3] who showed that on thermal decomposition the new compound yielded chlorine and oxygen in the volume ratio of 2 to 1. Since a vapor density of 86.92 was found, relative to hydrogen (=2), the formula Cl_2O was assigned to the gas.

Chlorine monoxide is a compound of considerable scientific interest. As a simple triatomic molecule belonging to the C_{2v} symmetry group, Cl_2O is a classical example of nonlinear XY_2 molecules and has therefore been extensively studied by spectroscopists. Also, conflicting reports on its stability have stimulated many investigations of its thermal decomposition as well as of its photolysis. Paradoxically, however, although this compound has been known for 140 years, its chemical reactivity has been relatively neglected. Indeed, its reactivity toward organic compounds has been the subject of only 14 publications. This neglect may be due to Balard's original report that chlorine monoxide gave violent reactions with all the organic compounds with which he brought it into contact, or to a general tacit assumption that all its reactions (in solution) would be the same as those of hypochlorous acid, of which it is the anhydride. The latter assumption is justifiable to a degree, since it has of late been suggested[4] that Cl_2O is the active species in the well-known reactions of HOCl with olefins and aromatic compounds. Indeed, it is to be noted that the conversion of HOCl into Cl_2O is believed to be the rate-controlling step in these reactions. Hence, one purpose of this review is to stimulate further research on the reactivity of chlorine monoxide with organic compounds, particularly on the mechanism of chlorination by HOCl and Cl_2O.

Another purpose is to examine comprehensively and critically the present state of knowledge of the chemistry of Cl_2O, in the light of growing industrial interest in this gas. For some years, chlorine monoxide has been made on a limited industrial scale as an intermediate in the manufacture of hypochlorite-based disinfectant powders,[5] but has had no other major use. Recently, however, Cl_2O has been found to be an effective reagent for the bleaching of wood pulp and textiles.[6,7] The use of chlorine monoxide in bleaching wood pulp promises not only to increase process efficiency, but also to significantly reduce stream pollution.

Thus, a review is timely, particularly since chlorine monoxide has hitherto only been the subject of short reviews in treatises of inorganic chemistry[8,9] and in the "Encyclopedia of Chemical Technology".[5]

It should be pointed out that in recent publications, Cl_2O is referred to as dichlorine monoxide; this name is more correct than chlorine monoxide and appears to be gaining currency.

[†] Present address: International Paper Co., Corporate Research & Development Division, P.O. Box 797, Tuxedo Park, N.Y. 10987.

* Author to whom correspondence should be addressed.

Nevertheless, in accordance with the bulk of the cognate literature, and with technological usage, the designation chlorine monoxide is retained in the present review.

II. Preparation

A. Mercuric Oxide Method

The laboratory technique[10,11] in widest current use for directly preparing gaseous chlorine monoxide is a reaction (eq 1) based essentially on Balard's original method[1,2]: a stream of chlorine, which may be diluted in an unreactive gas, is passed slowly (2.1[10] to 15 l./h[11]) through a column containing mercuric oxide thoroughly mixed with a suitable supporting material, and kept at 18–25 °C, preferably 20 °C.[10] This method gives very high levels (90+%) of conversion of chlorine into chlorine monoxide. At low flow rates of diluted chlorine, nearly quantitative conversion is reported.[10,11] Nevertheless, losses of yield can occur through the side reaction shown as eq 2, and, if they are to be minimized, several precautions must be observed, including: (1) adequate preparation of the mercuric oxide; (2) thorough mixing of the latter with its inert solid support; and (3) use of pure chlorine and diluent gas.

$$2Cl_2 + nHgO \rightarrow HgCl_2 \cdot (n-1)HgO + Cl_2O \quad (1)$$

$$2Cl_2 + 2HgO \rightarrow 2HgCl_2 + O_2 \quad (2)$$

It was recognized very early that proper preparation of the mercuric oxide was crucial for attaining a high level of conversion of chlorine into Cl_2O. The first workers in the field[1-3] used freshly precipitated, dried, yellow mercuric oxide, but soon recommended that it be heated for about 1 h at 300–400 °C before use. Later, the recommended temperature of pretreatment was reduced to 250 °C.[12,13] A subsequent investigation of the drying conditions led to the conclusion that heating above 300 °C for a long time was detrimental to the reactivity of the reagent.[14] At the same time it was found that commercially available mercuric oxide was generally unsuitable for the efficient production of Cl_2O, and tended to promote reaction 2 unless heated before use at a temperature between 100 and 200 °C.[14] These conclusions have been substantiated by other workers, and current practice calls for heating the mercuric oxide for 10 h at 125–130 °C.[10] In special cases, when Cl_2O of high purity is desired, the HgO can be degassed, either by conducting the preheating under reduced pressure[15] or by evacuating the flask containing the reagent, prior to adding pure chlorine.[16]

Mixing the mercuric oxide with an inert solid increases the surface of contact with chlorine and gives a further improvement in yield. The particles of inert material must be large enough to give a porous bed which will not impede the flow of gas. They should not exceed 1 cm in any dimension, and fines must be removed by screening through a 10-mesh sieve;[11] the optimum size of the particles was found to be 1–3 mm.[10] Materials proposed as the inert component include sand, potassium sulfate,[3] crushed glass tubing,[11] Kieselguhr,[17] pumice, and crushed building bricks.[10] The proportions of the mixture do not seem to be critical, but current practice tends to a greater volume of supporting material: for example, equal weights of HgO and glass,[11] or 1 vol of HgO for 4 vol of brick or pumice fragments.[10]

The gas with which the chlorine is diluted serves to moderate the reaction and to displace the high-density Cl_2O as it is formed.[18] Commercially available chlorine and diluents have usually been found satisfactory, but impurities sometimes cause low conversion ratios. Purification can be effected by bubbling the gases through 18 M H_2SO_4,[11] and further improved by passing the chlorine through anhydrous $CaCl_2$, and the air, or other diluent, through a column of granular KOH.[10] In a special instance, when very pure chlorine was required, it was prepared directly by the reaction of chlorine trifluoride, ClF_3, with sodium chloride.[15]

The gas emerging from the column of mercuric oxide contains chlorine monoxide diluted with inert gas, but often contaminated with various amounts of unreacted chlorine. Preliminary purification is achieved by condensing the Cl_2O in a trap cooled with mixtures of dry ice and alcohol,[12,13] acetone,[11] or carbon tetrachloride–chloroform (1:1).[10] At a low flow rate (2.1 l./h) of an incoming mixture of Cl_2 and N_2 (1:1), a trap cooled at −60 °C will quantitatively condense the product Cl_2O, with only traces of chlorine present in the condensed liquid.[10] Further purification can be achieved by passing the gas over phosphorus pentoxide[13] or dry calcium nitrate, or by fractional distillation at low temperature under reduced pressure. By maintaining the liquid under vacuum at −80 °C, most of the contaminating chlorine can be pumped off.[19]

If the presence of diluent gas is undesirable, high conversion of pure chlorine can be achieved by passing it through a very long tube (25 m) coated with a layer of mercuric oxide.[20] Alternatively, the reaction vessel may be a fractionating column, with HgO on Kieselguhr spread on its plates; the Cl_2O formed is condensed after each cycle, and the unreacted chlorine is recycled.[15,17]

When only small quantities of Cl_2O are required, the flow-through technique need not be employed. Instead, a static system[16] can be used. In one method, a predetermined quantity of chlorine is condensed at −196 °C into an evacuated flask containing HgO. The reaction is left to proceed overnight at the temperature of a dry ice–trichloroethylene bath. After distillation of the mixture at low temperature, Cl_2O is obtained in 60% yield. A higher yield (94%) is reported from another method[6] wherein a mixture of air and chlorine is introduced into an evacuated flask containing a mixture of yellow mercuric oxide and phosphorus pentoxide. The chlorine–air mixture is agitated by means of a motor-driven stirrer, and additional air is periodically admitted to replace the chlorine consumed. The Cl_2O–air mixture is then transferred to an evacuated flask where it can be diluted and stored.

The reaction of chlorine with mercuric oxide can also be used to prepare solutions of Cl_2O in carbon tetrachloride. Mercuric oxide, pretreated under optimal conditions (10 h at 120–130 °C), is added to a solution of Cl_2 in CCl_4 at room temperature.[11,14,21] The reaction is fast, and, after separation of the basic mercuric chloride, a stable solution of Cl_2O in CCl_4 is obtained. Yields are in the range of 90–95%,[14,21] provided that pure CCl_4 is used. An elaborate method for purifying the solvent has been described,[22] but a simpler method, requiring only distillation of commercial AR CCl_4 over phosphorus pentoxide, is reported to give satisfactory results.[23]

At the end of the reaction, whatever the technique of preparation, the mercuric oxide may be regenerated[11] from the residual basic mercuric chloride ($HgCl_2 \cdot nHgO$) by treatment with an excess of alkali; a pH of 10.5 is said to be optimal for the final supernatant.[14] The temperature must be kept from rising during the addition of alkali, since mercuric oxide precipitated at 102 °C showed a marked loss of reactivity. The recovered HgO is washed extensively and finally dried at 120–130 °C.[11] The reactivity of the oxide is said to increase after each regeneration.[10]

B. Sodium Carbonate and Allied Methods

In the sodium carbonate method used industrially for preparing chlorine monoxide, the well-known equilibrium of the reversible hydrolysis of chlorine (eq 3) is displaced to the right by removing hydrochloric acid as sodium chloride. Provided that only a small amount of water is present, the solubility of HOCl is rapidly exceeded and chlorine monoxide is evolved. Although sodium carbonate is generally used in this reaction, other alkali metal carbonates and other alkaline compounds of alkali metals[25] (such as phosphates, stannates, silicates, aluminates, or oxides) may be employed. Increasing the surface of gas–solids contact by grinding the alkali salts and agitating the bed has been found to be beneficial.[24,25] The reaction with sodium carbonate is described by eq 4 and 5.

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl \qquad (3)$$

$$2Cl_2 + 2Na_2CO_3 + H_2O \rightarrow Cl_2O + 2NaHCO_3 + 2NaCl \qquad (4)$$

$$2Cl_2 + 2NaHCO_3 \rightarrow Cl_2O + 2CO_2 + 2NaCl \qquad (5)$$

Under the optimal conditions of reaction,[24] sodium carbonate, containing approximately 10% of water, is allowed to fall slowly down a reaction tower and contacted with an upward flow of chlorine diluted to about 25% in a gas such as air, nitrogen, or carbon dioxide. The humidity in the reaction zone must be maintained at around 10%, either by saturating the incoming gas with water or by injecting steam into the reactor at regular intervals. The temperature of the reaction zone is preferably maintained at about room temperature (20–30 °C), but may be raised to as high as 200 °C.

The reaction can be adapted to the preparation of solutions of Cl_2O in carbon tetrachloride.[11,24]

Chlorine monoxide can also be formed when chlorine is brought into contact with dry carbonates or bicarbonates at temperatures above 150 °C, preferably 200 °C.[24]

C. Preparation from Hypochlorous Acid Solutions

Since, as shown by distribution experiments, Cl_2O is several times more soluble in CCl_4 than in water,[26] solutions of the gas may be prepared by liquid–liquid extraction (shaking in a separatory funnel) of aqueous solutions of HOCl.

Pure, anhydrous, liquid chlorine monoxide can be prepared by distilling, in vacuo over HgO, a 25% aqueous solution of hypochlorous acid.[26] The distillate is collected in three receivers in series, cooled at 0, −20, and −80 °C, respectively. The first two receivers condense only the initial 25% hypochlorous acid solution, while the third condenses the Cl_2O.

Pure gaseous Cl_2O can also be prepared by the classical method of treating concentrated solutions of HOCl with anhydrous calcium nitrate.[1]

An alternative method for producing the gas is to pass a stream of air through an aqueous solution of HOCl. The nature of the entities present in the emerging stream of wet air is a matter of controversy and is discussed later (see section IV.C). However, when the air stream is dried over anhydrous calcium nitrate, chlorine monoxide is obtained.[27,28]

III. Analysis

An iodometric method is generally used for the titrimetric determination of Cl_2O, which reacts with potassium iodide to yield 4 equiv of iodine and 2 equiv of hydroxide ion (eq 6). Since conditions must be acidic for the titration of iodine with thiosulfate, a known excess of acid can be added. After titration, the residual acid can be back-titrated with standard alkali. The possibility of back-titration is useful when the Cl_2O is to be determined in the presence of chlorine, which does not generate hydroxide ion on reaction with iodide (eq 7). Thus the iodometric titration gives the sum of chlorine monoxide and chlorine, and the back-titration gives a measure of Cl_2O alone.

$$Cl_2O + 4I^- + H_2O \rightarrow 2OH^- + 2Cl^- + 2I_2 \qquad (6)$$

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2 \qquad (7)$$

Several reagents have been proposed for the back-titration. Standard alkali and methyl orange indicator have been used,[21] as well as 0.1 N $Ba(OH)_2$ with phenolphthalein.[29] However, the simplest method to estimate the excess of acid is to add a slight excess of potassium iodate solution after the first iodometric titration (eq 8), and then titrate the liberated iodine with additional thiosulfate.[30]

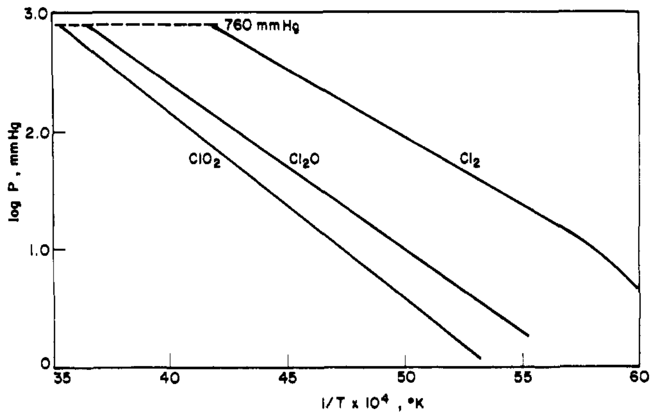


Figure 1. Vapor pressure of chlorine and chlorine oxides.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (8)$$

In addition to titration, several instrumental methods are used for the analysis of chlorine monoxide, although they have not all been fully explored and developed.

The use of vapor-phase chromatography has been reported.[16] The gas chromatograph employed was specially built to resist highly corrosive gases (Cl_2, ClO_2, F_2, ClF, ClF_3), all the parts being made of stainless steel, Monel, or nickel. The stationary phase in the column was a halocarbon oil, 13-21, on a Kel-F300 support.[31]

As to other instrumental methods, Spurny[32] has reported that the oxides of chlorine, including Cl_2O, can be photolyzed quantitatively to chlorine which can then be determined spectrophotometrically. Infrared spectroscopy (section V.F) is a potentially useful method for the direct determination of Cl_2O, but a possible disadvantage is that, especially at low concentrations of the gas, excessively long cells may be required to produce absorption bands intense enough to be useful. The ultraviolet spectrum of Cl_2O has been described (section V.E) but has not been used for quantitative measurements; the photolytic decomposition of Cl_2O by ultraviolet light (section VI.A) is likely to have an adverse effect on precision and reproducibility.

IV. Physical Properties

A. General

At ordinary temperatures, chlorine monoxide is a gas, pale orange-yellow with a slight greenish tinge. Its vapor density has been reported as 2.977[33,34] and 3.007,[35] air being taken as unity. It condenses to a reddish-brown liquid whose vapor pressures have been measured by means of a mercury manometer protected by a dry air buffer.[13] The results, plotted in Figure 1, were in agreement with eq 9 (p, pressure in mmHg; T, temperature in K) in the range of 173–288 K. The figure also shows corresponding data for Cl_2[36] and ClO_2,[37] the most common contaminants of Cl_2O. It illustrates how purification of the latter by fractionation will be easy when the impurity is chlorine, but difficult when it is chlorine dioxide.

$$\log p = (-1373/T) + 7.87 \qquad (9)$$

The boiling point of Cl_2O has been reported as 3.8 °C,[26] but was subsequently determined as 2.0 °C, at 760 mmHg from the vapor pressure data.[13] The higher value, now unacceptable, was attributed[13] to the frequently observed superheating of the liquid.

By a method of correlating increments,[38] the critical constants

TABLE I. Thermodynamic Functions for the Reaction $Cl_2(g) + \frac{1}{2}O_2(g) \rightarrow Cl_2O(g)$

T, K	$\Delta H°_T$, kcal mol^{-1}	$\Delta G°_T$, kcal mol^{-1}	$\Delta S°_T$, cal deg^{-1}	$S°_T$, cal deg^{-1}	Ref
291	18.26				42
298.16	18.26	21.207	−9.93	67.9	43
273.16	18.10	21.950	−14.06	63.8	44
298	23.50	21.870	+5.47	83.3	45

of 15 inorganic compounds of Cl, O, and N were calculated.[39] The results for Cl_2O, based on increments for O and Cl computed from experimental values of the thermodynamic properties of O_2, O_2F, ClF_3 and $FClO_3$, were: t_c = 192.2 °C, p_c = 64.9 atm, v_c = 169 cm^3/mol, d_c = 0.519 g/cm^3. It is difficult to assess the predictive power of this method, since very few experimental data were available for comparison with the calculated constants for most of the 15 compounds. Nevertheless, the calculated heat of vaporization of Cl_2O, 5588 cal/mol, agrees moderately well with the experimental value of 6200 cal/mol.[13] By the same method of calculation, eq 10 represents the equation of state for Cl_2O, in its van der Waals approximation, where p is pressure in atmospheres and V is volume in cm^3.

$$p = \frac{nRT}{(V - 73.5n)} - \frac{n^2 \times 9.47 \times 10^{-6}}{V} \qquad (10)$$

The melting point of Cl_2O was found to be −116 ± 1 °C, when determined with a standard pentane thermometer. Subsequent investigation[40] on freshly prepared Cl_2O, dried over P_2O_5 and purified by fractionation, and with a carefully calibrated copper–constantan thermocouple, gave a freezing point of −120.6 °C.

B. Thermodynamic Properties

1. Heat of Vaporization

The straight-line slope of the logarithm of the vapor pressure plotted against the reciprocal of the absolute temperature, in the range of 173–288 K, has given the latent heat of vaporization of Cl_2O as 6.2 kcal/mol,[13] which agrees with a later, independently determined value[41] of 6.3 ± 0.2 kcal/mol. The corresponding Trouton's constant ($\lambda v/T_b$) is therefore 22.5 cal deg^{-1} mol^{-1}, and indicates very little, if any, association of Cl_2O in the liquid state.

2. Heat of Formation

Table I shows various published values of the heat of formation of chlorine monoxide, and the thermodynamic functions derived from them.

From the heat of solution, at 18 °C, in a large excess of water, the heat of formation of $Cl_2O(g)$ was calculated as $\Delta H°_{291}$ = 18.26 kcal/mol.[42] This value—as well as the heat of solution of Cl_2O in CCl_4 computed from vapor pressure measurements, the free energies of chlorine hydrolysis,[45] solution of chlorine in water, formation of HCl(aq) and H_2O(l), hydrolysis of Cl_2O, and partition of Cl_2O between water and CCl_4[46]—was used to calculate the free energy of formation of Cl_2O: $\Delta G°_{298}$ = 21.207 kcal/mol. The corresponding entropy of gaseous Cl_2O at 25 °C and 1 atm is 67.9 cal deg^{-1}.[43]

These derived quantities agree rather well with those calculated[44] by taking 18.1 ± 0.3 kcal/mol as the best value for the heat of formation: $\Delta G°_{273.16}$ = 21.95 kcal/mol; $S°_{298.16}$ = 63.76 cal deg^{-1}.

The figures in the last row of Table I do not accord with the others. Here, the heat of formation was derived[45] by considering the enthalpies and free energies of the following processes: H_2O(l) formation, HOCl(aq) formation, and dissolution of Cl_2O in water (calculated from vapor pressure measurements). This gave $\Delta H°_{291}$ = 23.5 kcal/mol, and the corresponding $\Delta G°_{298}$ = 21.87 kcal/mol. The consequent entropy for Cl_2O in the standard state, 83.3 cal deg^{-1}, is undoubtedly too high (see section IV.A.3), probably owing to the large value found for $\Delta H°$. Another possible source of error is that the heats of solution used in the computation of $\Delta H°$ are of doubtful validity; they differ appreciably from those found by other workers and exhibit an anomalously large dependence on temperature.

Nevertheless, rather high values of the heat of formation were obtained by measuring the amount of heat liberated from the explosion of Cl_2O: 21.735 ± 0.560,[47] 20.050 ± 1.000,[48] and 25.100 ± 0.100[49] kcal/mol.

3. Thermodynamic Functions from Spectroscopic Data

Various authors have used spectroscopic data to calculate the molar thermodynamic functions such as heat content, free energy, entropy, and heat capacity. In computing these functions for an ideal gaseous state at 1 atm, a rigid rotator, harmonic oscillator model was assumed; nuclear spins and isotopic mixing were neglected. Table II shows the functions calculated for T = 298.16 K, as well as the frequencies and product of the three principal moments of inertia used in the computation of partition functions. It is to be noted that the values of $S°$ agree best with that in the third line of Table I.

Tabulations of these thermodynamic functions over a large range of temperatures can be found in the original papers.

C. Solubility

1. In Water

Gaseous chlorine monoxide readily dissolves in water (eq 11) where it hydrolyzes as shown in eq 12. Its solubility, at a given partial pressure of solute and at temperatures between 0 and 20 °C, may be conveniently estimated from the nomograph in Figure 2.[54] The nomograph was derived from previously pub-

TABLE II. Thermodynamic Functions of Cl_2O, Calculated from Spectroscopic Data

		Reference				
		50	51	44	52	53
Absorption frequencies, cm^{-1}	ν_1	688	688	684	640	630.7
	ν_2	320	320	320	300	296.4
	ν_3	969	969	973	686	671
Product of moments of inertia, $I_A \cdot I_B \cdot I_C$ (× 10^{-114})		1.165		1.173	1.171	
$(H_0 - E°_0)/T$, kcal deg^{-1} mol^{-1}		9.12	9.114	9.12		9.23
$-(G_0 - E°_0)/T$, kcal deg^{-1} mol^{-1}		54.51	55.014	54.52		53.76
$C_p°$, cal deg^{-1} mol^{-1}		10.85	10.842	10.90	11.427	11.20
$S°$, cal deg^{-1} mol^{-1}		63.63	64.128	63.64	64.019	62.99

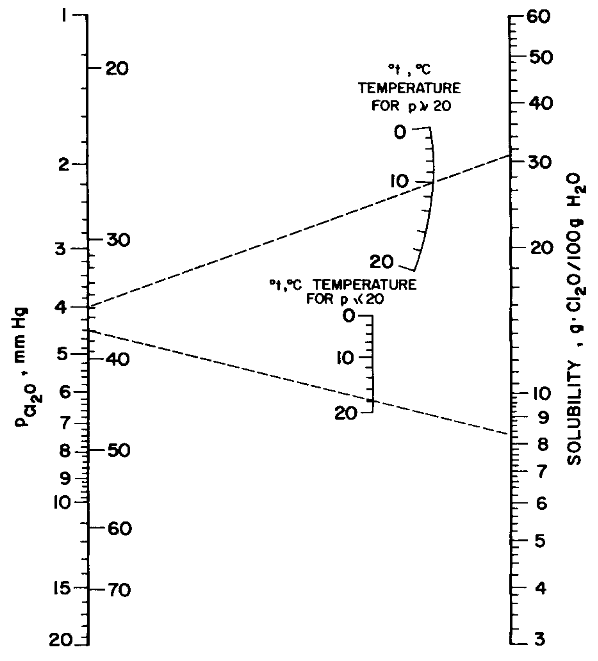


Figure 2. Nomograph for the solubility of chlorine monoxide in water.

lished[45] measurements of vapor pressure. It was the observation[26] that Cl_2O could be extracted by carbon tetrachloride from a concentrated (aqueous) hypochlorous acid solution which suggested that reaction 11 represents an equilibrium condition.

$$Cl_2O(g) \rightleftarrows Cl_2O(aq) \quad (11)$$

$$Cl_2O(aq) + H_2O(l) \rightleftarrows 2HOCl(aq) \quad (12)$$

The heat of solution of chlorine monoxide in a large excess of water has been determined calorimetrically as 9.439 kcal/mol at 18 °C[42] and 8.940 kcal/mol at room temperature.[55] The thermodynamic functions reported in Table III were calculated by extrapolating to zero molality the curves obtained by plotting the measured vapor pressure of Cl_2O against the molality. This procedure also gave the equilibrium constant for eq 11.

The values of ΔH in this table differ significantly from those found by direct, calorimetric measurements.[42,55] They also exhibit an unusually large temperature dependence. Critical reexamination[56] of the treatment of the vapor pressure measurements[45] has taken into account the equilibrium of hydrolysis of Cl_2O (eq 12) and has given Henry's constant for Cl_2O over its aqueous solution as 0.00937 ± 0.00005 (P_{Cl_2O} expressed in mmHg). Thus, the true solubility of Cl_2O is five times greater than that of chlorine. From the best available values for the heats of formation of HOCl(aq), Cl_2O(g), and H_2O(l), the heat of solution of Cl_2O in water was computed as 9.44 kcal/mol, in good agreement with values determined by calorimetry.

Liquid Cl_2O and water are only partially miscible. Figure 3 shows the temperature-concentration diagram for the system. When the fraction of Cl_2O exceeds 11.7 mol % (39% Cl_2O by weight), a solid phase forms, which has the composition $HOCl{\cdot}2H_2O$. When chlorine monoxide and water are mixed in stoichiometric proportions to give HOCl, two liquid phases are formed which, on freezing, give the hydrate $HOCl{\cdot}2H_2O$ as the solid phase.[40]

The equilibrium constant K for the hydration of Cl_2O (eq 13) and the partition coefficient R of Cl_2O between water and carbon tetrachloride (eq 14) can be computed by resolving a system of two equations formed by substituting in eq 13 and 14 experimental values for [HOCl] + [Cl_2O(aq)] and [$Cl_2O(CCl_4)$] for two experiments at different initial concentrations of Cl(I) compounds in the aqueous phase. Goldschmidt[26] obtained values of 1/1040 for $K_{273.16}$ and 8 for R. However, Roth[46] later remarked that the experimental values selected by Goldschmidt for his computation were obtained for only slightly different initial concentrations of Cl(I) compounds, leading to gross errors in the determination of K and R. Using Goldschmidt's experimental results, Roth computed lower values, i.e., $K_{273.16°} = 1/282$ and $R = 2.22$, by selecting sets of experiments with a wider range of initial concentrations.

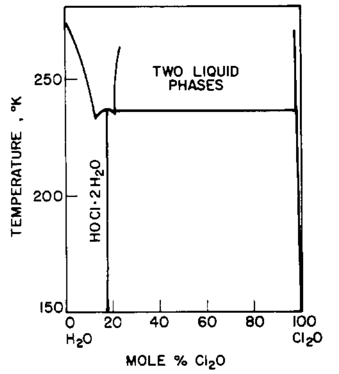


Figure 3. Temperature-concentration diagram for the system chlorine monoxide-water.

TABLE III. Heat of Solution of 1 Mol of Cl_2O in an Excess of Water

Temp, K	ΔH_T, kcal/mol	ΔG_T, kcal/mol
278	9.3	
283	11.4	
291	16.0	3.73
298		3.35

$$2HOCl(aq) \rightleftarrows Cl_2O(aq) + H_2O(l) \quad (13)$$

$$K = [Cl_2O(aq)]/[HOCl]^2$$

$$Cl_2O(aq) \rightleftarrows Cl_2O(CCl_4) \quad (14)$$

$$R = [Cl_2O(CCl_4)]/[Cl_2O(aq)]$$

The value $K_{273.16} = 1/282$ was used by Roth[46] to estimate K_{292} as 1/115 and the heat of solution of chlorine monoxide in water as 8.34 kcal/mol in reasonable agreement with the experimental value of 8.94 kcal/mol.[55]

Figure 4 summarizes the results of measuring the vapor pressures of chlorine(I) compounds above aqueous hypochlorous acid in very dilute solutions (10^{-3}–10^{-1} mol in 1000 g of H_2O) at 15 °C,[57] in dilute solutions (10^{-1}–2 mol in 1000 g of H_2O) at 10 and 20 °C,[58] and concentrated solutions (1–20 mol in 1000 g of H_2O) at 3.46, 6.00, 9.92, 16.00, and 19.98 °C.[45] Despite the differences in experimental methods, the results of Secoy and Cady,[45] obtained under static conditions, and those of Ourisson and Kastner,[58] obtained under dynamic conditions, are in very good agreement.

The authors clearly disagree, however, in the interpretation of their results. Since solid HOCl could not be prepared at low temperature, Secoy and Cady[45] inferred that HOCl could not exist in the gaseous state and, therefore, that the vapor above an aqueous solution of HOCl should consist of only Cl_2O and H_2O. This point of view has also been advanced by Noyes and Wilson[27] who passed a stream of air through 0.27 N hypochlorous acid and measured the weight of water trapped by anhydrous calcium nitrate, and of chlorine monoxide trapped in an NaOH solution. Since the weight of water collected in the drying tube corresponded almost exactly to the theoretical amount in the given volume of saturated air, Noyes and Wilson concluded that the chlorine(I) species present in the vapor is Cl_2O and not HOCl.

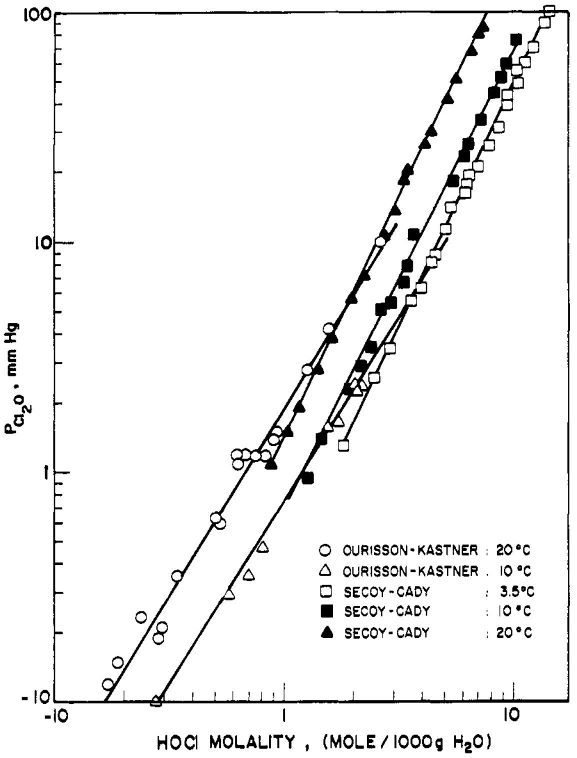


Figure 4. Vapor pressure of chlorine(I) compounds above their aqueous solution.

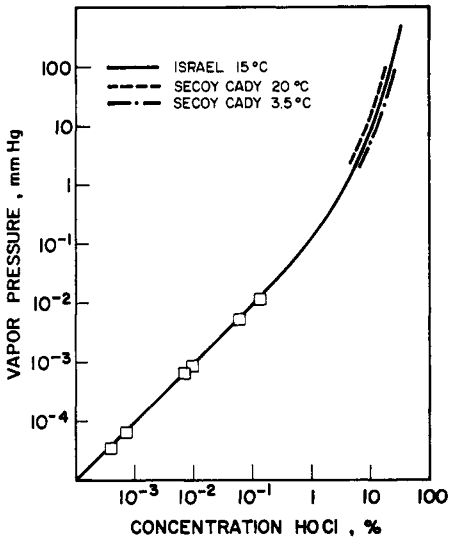


Figure 5. Vapor pressure, expressed as HOCl, above aqueous solutions of chlorine(I) compounds, over a wide range of concentrations.

Indeed, the titrations of the gas collected in the sodium hydroxide showed that Cl_2O and not HOCl had been trapped in it. However, this result was to have been expected, since any HOCl which might have initially been present in the vapor-laden air would have been dehydrated to Cl_2O on passage through the tube of anhydrous calcium nitrate.[1]

The results of Noyes and Wilson clearly exclude the hypothesis that all Cl(I) compounds in the vapor are present as HOCl. However, their experiment II can be reevaluated in the light of subsequent published results,[58] and then it is equally clear that a small amount of HOCl might be present. Thus, when one applies to experiment II the equilibrium constant for eq 15, one finds that approximately 2 mg of water would be combined with Cl_2O as HOCl and would contribute to the weight of water (63 mg) collected in the drying tube. This difference of 3% could easily escape observation, particularly since the efficiency of drying does not seem to be absolute: the weights of water actually found were consistently 1–2% less than theoretical.

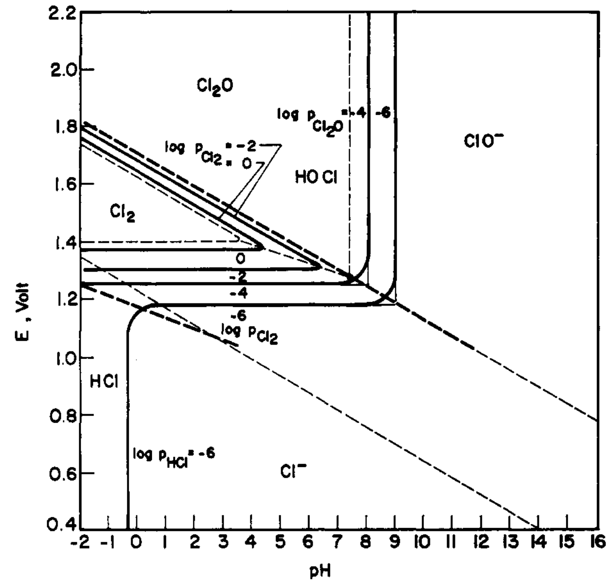


Figure 6. Stability of chlorine(I) compounds in aqueous solutions.

TABLE IV. Values of K_1 and K_2 in Eq 17

Temp, °C	$2K_1$	K_2
10	0.42	0.24
20	1.30	0.70
30	3.74	1.89

The general consensus among authors[57-60] who have written on this subject is that $Cl_2O(g)$ and HOCl(g) coexist in the vapor phase above an aqueous solution of HOCl, the former predominating at high concentrations, and the latter at low concentrations. Figure 5 provides experimental support for this view by presenting the vapor pressure of Cl(I) compounds above a solution of HOCl plotted against the concentration (in terms of HOCl) of the solution, over a wide range of concentration. Among very dilute solutions, the vapor pressure varies linearly with the concentration, thus suggesting a predominance of HOCl in the vapor phase. As the concentration increases, the curve deviates from linearity and shows the increasing presence of Cl_2O. The evaporation process, then, takes place according to eq 15 and 16.[58] The partial pressure of chlorine(I) compounds above the solution (the concentration of which is expressed in terms of HOCl) is given by eq 17. Computed values for K_1 and K_2, at different temperatures, are reported in Table IV.[58]

$$2\mathrm{HOCl(aq)} \xrightleftharpoons{K_1} \mathrm{Cl_2O(g)} + \mathrm{H_2O(l)} \qquad (15)$$

$$\mathrm{HOCl(aq)} \xrightleftharpoons{K_2} \mathrm{HOCl(g)} \qquad (16)$$

$$P_{\mathrm{Cl(I)}} = 2P_{\mathrm{Cl_2O}} + P_{\mathrm{HOCl}} = 2K_1[\mathrm{HOCl(aq)}]^2 + K_2[\mathrm{HOCl(aq)}] \qquad (17)$$

Despite all of the foregoing argument, it must be recognized that the presence of HOCl in the vapor above its solution has not been established by an unambiguous proof, as might be provided by direct spectroscopic measurement. Such proof would be highly desirable.

Not only the composition of the vapor but also the composition and stability of solutions of Cl_2O in water, as a function of pH, are of considerable technical interest. Since the solutions are those of the very weak hypochlorous acid (pK = 7.5), we are dealing with solutions of HOCl and OCl^- in equilibrium with Cl_2O at a particular partial pressure above them (Figure 6). Many complex reactions and equilibria can and do occur in these solutions and are further complicated when chloride ion is present.[61]

Consideration of the relative positions of the stability domains of HOCl and OCl^-, as compared with those of water, shows that hypochlorous acid and hypochlorites—while appearing to decompose to oxygen and to chlorine or chloride—actually oxidize water, which is the source of the evolved oxygen. As shown by eq 19–21, the reactions vary with the pH of the solution. The relatively high stability of neutral and alkaline solutions of hypochlorous acid and hypochlorites arises from the slowness of the oxidation of water under alkaline conditions, which in turn is related to the virtual irreversibility of the oxidation reaction (eq 18)

(a) pH $<\approx 4$:

$$\begin{array}{rll} 2H_2O & \longrightarrow O_2 + 4H^+ + 4e^- & (18)\\ 4HOCl + 4H^+ + 4e^- & \longrightarrow 2Cl_2 + 4H_2O & (19)\\ \hline 4HOCl & \longrightarrow 2Cl_2 + O_2 + 2H_2O & \end{array}$$

(b) pH ≈ 3.3–7.5:

$$\begin{array}{rll} 2HOCl + 2H^+ + 4e^- & \longrightarrow 2Cl^- + 2H_2O & (20)\\ 2H_2O & \longrightarrow O_2 + 4H^+ + 4e^- & (18)\\ \hline 2HOCl & \longrightarrow 2Cl^- + O_2 + 2H^+ & \end{array}$$

(c) pH $>\approx 7.5$:

$$\begin{array}{rll} 2OCl^- + 4H^+ + 4e^- & \longrightarrow 2Cl^- + 2H_2O & (21)\\ 2H_2O & \longrightarrow O_2 + 4H^+ + 4e^- & (18)\\ \hline 2OCl^- & \longrightarrow 2Cl^- + O_2 & \end{array}$$

When aqueous solutions of HOCl contain chloride ions, and are acidic, the slow oxidation of water is replaced by the rapid oxidation of the chloride ions to chlorine (eq 22). As shown by eq 23, the stability of an acidic hypochlorous acid solution will decrease with increasing concentrations of chloride ion.

$$\begin{array}{rll} 2Cl^- & \longrightarrow Cl_2 + 2e^- & (22)\\ 2HOCl + 2H^+ + 2e^- & \longrightarrow Cl_2 + 2H_2O & (23)\\ \hline 2HOCl + 2Cl^- + 2H^+ & \longrightarrow 2Cl_2 + 2H_2O & \end{array}$$

In equilibria involving the higher oxyacids of chlorine, both hypochlorous acid and hypochlorites can decompose into chlorites and chlorides, according to eq 24 and 25. When chloride ions are present, the domain of stability of chlorates completely overlaps that of ClO^- and HOCl. Hence these latter

$$\begin{array}{rll} HOCl + H^+ + 2e^- & \longrightarrow Cl^- + H_2O & (20)\\ HOCl + H_2O & \longrightarrow HClO_2 + 2H^+ + 2e^- & (24)\\ \hline 2HOCl & \longrightarrow HClO_2 + Cl^- + H^+ & \end{array}$$

$$\begin{array}{rll} OCl^- + 2H^+ + 2e^- & \longrightarrow Cl^- + H_2O & (21)\\ OCl^- + H_2O & \longrightarrow ClO_2^- + 2H^+ + 2e^- & (25)\\ \hline 2OCl^- & \longrightarrow Cl^- + ClO_2^- & \\ OCl^- + 2HOCl & \longrightarrow ClO_3^- + 2Cl^- + 2H^+ & (26) \end{array}$$

species are thermodynamically unstable toward ClO_3^- and Cl^- and tend to exhibit reaction 26, which, in practice, does not have an appreciable rate at 25 °C. However, at higher temperature (50 °C), the rate increases sufficiently to become significant.

2. In Carbon Tetrachloride

TABLE V. Dielectric Constant, ϵ, and Molar Polarization, P, for Cl_2O in Dilute CCl_4 Solutions[55]

Temp, °C	Mole fractions (ϵ)					
	0.00597	0.01197	0.01952	0.02838	0.0390	P, cm^{-3}
−18	2.3160	2.3196	2.3239	2.3294	2.3367	25.42
−8	2.2952	2.2988	2.3025	2.3078	2.3146	24.56
3	2.2728	2.2761	2.2796	2.2843	2.2904	24.16
14	2.2505	2.2535	2.2568	2.2609	2.2662	23.72
24	2.2305	2.2330	2.2360	2.2399	2.2441	23.14

As determined by a dynamic method,[43] the vapor pressure of Cl_2O above dilute solutions in CCl_4 obeys Henry's law. The constants, 1830 mmHg/mol % at 25 °C, and 662 mmHg/mol % at 0 °C, have permitted the computation of the thermodynamic function for eq 27:

$$Cl_2O(g) \rightleftarrows Cl_2O(CCl_4) \qquad (27)$$

$$\Delta G°_{298} = -8.864 \text{ kcal/mol};\ \Delta H° = 6.59 \text{ kcal/mol}$$

Combining these with other thermodynamic data has given the corresponding functions for the formation of Cl_2O in CCl_4 (eq 28):

$$Cl_2(g) + \tfrac{1}{2}O_2(g) \rightarrow Cl_2O(CCl_4) \qquad (28)$$

$$\Delta G°_{273} = 20.71 \text{ kcal/mol};\ \Delta H°_{298} = 24.85 \text{ kcal/mol}$$

The heat of dilution of Cl_2O by CCl_4, determined from 0.5 to 3×10^{-6} M, was close to zero.[62] It was therefore concluded that the heat of formation of Cl_2O in CCl_4, as calculated from the heat of reaction of Cl_2O (CCl_4; 0.45 M) with HO_2^-(aq)[63] and available thermodynamic data, would also be the heat of formation of Cl_2O in CCl_4 at infinite dilution. Accordingly, ΔH_T, the heat of formation of Cl_2O in CCl_4, was found to be represented by eq 29. Substituting for ΔH_T in the van't Hoff equation and integrating gave $\Delta G°_T$, the free energy of formation (eq 30). The integration constant, I, was evaluated as −2.3102 by combining the free energies of formation of Cl_2O(g) and of solution of Cl_2O(g) in CCl_4 at 298 K to give a value of $\Delta G°_{298}$.

$$\Delta H_T = 30.52 - 0.4546T + 0.00141T^2 \text{ (kcal/mol)} \qquad (29)$$

$$\Delta G°_T = 30.52 + 0.4546T \ln T - 0.00141T^2 + IT \text{ (kcal/mol)} \qquad (30)$$

These equations gave the following values for the thermodynamic constants of Cl_2O formation in CCl_4 at 298 K: $\Delta H_{298} = +12.57$ kcal/mol, $\Delta G°_{298} = +21.54$ kcal/mol, $\Delta S_{298} = -30.1$ cal deg^{-1}.

These values are considerably lower than those previously reported;[43] they give[62] 47.69 cal deg^{-1} for the entropy content of Cl_2O in CCl_4 at 298 K—much lower than $S°_{298}$ = 63–64 cal deg^{-1} derived from spectroscopic data for Cl_2O gas (see Table II). This difference is too large to be attributable to the entropy of mixing, which, in this practically ideal solution, should be small. Therefore, the published thermodynamic functions for Cl_2O formation in CCl_4 solution[62] should be accepted only with reservations.

V. Structure and Spectrochemistry

A. Dipole Moment

Chlorine monoxide is a nonlinear molecule, with a dipole moment of $(0.78 \pm 0.08) \times 10^{-8}$ esu, as calculated from the temperature dependence of its molar polarization.[64] The supporting experimental data (Table V) show the dielectric constants of dilute solutions of Cl_2O in CCl_4, as determined at various concentrations and at temperatures from −20 to 25 °C. The uncertainty of the measurements was given as 0.01%. Molar polarizations, P, were computed from densities measured in a quartz dilatometer.

TABLE VI. Mass Spectra of Cl_2O

Reference Mass spectrometer		Fisher[65] Modified AEI-MS2[66]	Freeman, Phillips[67]	Cordes, Smith[68] "Time of Flight" Bendix Model 12
m/e	Ion	% of the most abundant species		
16	O^+	NR[a]	2.8	0.88
17	OH^+	NR	1.3	NR
17.5	$^{35}Cl^{2+}$	NR	NR	0.50
18	H_2O^+	NR	3.4	NR
18.5	$^{37}Cl^{2+}$	NR	NR	0.17
28	N_2^+ CO^+	NR	6.0	NR
32	O_2^+	<0.07	NR	NR
35	$^{35}Cl^+$	<0.7	58.3	25.0
36	$(H^{35}Cl)^+$	NR	23.1	NR
37	$^{37}Cl^+$	<0.7	18.7	7.8
38	$(H^{37}Cl)^+$	NR	7.4	NR
44	CO_2^+	NR	7.2	NR
51	$(^{35}ClO)^+$	100.0	100.0	100.0
52	$(H^{35}ClO)^+$	NR	9.2	<1.0
53	$(^{37}ClO)^+$	33.4	32.0	31.2
54	$(H^{37}ClO)^+$	NR	2.9	<1.0
70	$(^{35}Cl^{35}Cl)^+$	5.4	15.9	9.0
72	$(^{35}Cl^{37}Cl)^+$	3.6	10.2	5.7
74	$(^{37}Cl^{37}Cl)^+$	0.5	1.6	0.97
86	$(^{35}ClO^{35}Cl)^+$	43.5	41.5	39.1
88	$(^{35}ClO^{37}Cl)^+$	28.3	26.5	25.7
90	$(^{37}ClO^{37}Cl)^+$	4.7	4.2	4.5
Electron energy (eV)		NR	50	70

[a] NR, not reported.

TABLE VII. Geometry of Cl_2O Molecule

d_{ClO}, Å	$d_{Cl\cdots Cl}$, Å	$\alpha = \angle ClOCl$, deg	Experimental method	Ref
1.71 ± 0.02	2.82 ± 0.02	111 ± 2	Electron diffraction	69
1.68 ± 0.03	284 ± 0.03	115 ± 4	Electron diffraction	70
1.70_1 ± 0.02	279_1 ± 0.02	110.8 ± 1	Electron diffraction	19
1.701		110.8	Electron diffraction	71
1.701		110.3	Electron diffraction	72
1.693 ± 0.003	2.795 ± 0.004	111.2 ± 0.03	Electron diffraction	73
1.70038 ± 0.00069		110.86 ± 0.04	Microwave spectroscopy	74
1.70038 ± 0.00043		110.96 ± 0.08		

B. Ionization Potential–Mass Spectroscopy

By means of mass spectrometry, the ionization potential of chlorine monoxide has been measured as 11.16 ± 0.10 eV. The appearance potential of the predominant fragment, $(ClO)^+$, was found to be 12.5 ± 0.1 eV, giving by calculation 32.3 ± 2 kcal/mol[65,66] for the dissociation energy of the Cl–OCl bond.

Table VI shows that the reported mass spectra of chlorine monoxide are in fair agreement, considering the differences in experimental conditions. Small discrepancies in the results can be attributed to impurities in the Cl_2O. Protonated species in the spectrum reported by Freeman and Phillips[67] are probably due to the presence of water and HOCl, and perhaps to products formed in reactions with the phosphoric acid coating on the walls of the spectrometer.

The spectra have shown that the dissociation of Cl_2O yields Cl^+ as a real fragment, its peak intensity being independent of time and of sample temperature.[68]

C. Molecular Geometry

The geometric characteristics of the Cl_2O molecule have been determined from both electron diffraction studies[19,69–73] and microwave spectroscopy.[74] The two methods have given very good agreement (Table VII) around the values of $d_{Cl-O} = 1.70$ Å, $d_{Cl\cdots Cl} = 2.79$ Å, and $\angle ClOCl = 110.8°$.

D. Photoelectron Spectroscopy

The relatively new technique of photoelectron spectroscopy (PES) permits the direct measurement of the energies required to remove valence shell electrons from atoms and molecules and provides information on the bonding characteristics of orbitals (for review, see ref 75). As applied to the chlorine monoxide molecule,[76] the PES technique has given the first ionization potential, under adiabatic ionization conditions, as 10.94 eV, which compares favorably with the potential of 11.16 eV found by mass spectroscopy.[65]

The first PES band shows a vibrational peak structure assigned to both ν_1 and ν_2. Since these frequencies in the ionized molecule ($\nu_1 = 670 \pm 40$ cm^{-1}; $\nu_2 = 300 \pm 40$ cm^{-1}) are larger than in the neutral molecule ($\nu_1 = 631$ cm^{-1}; $\nu_2 = 296$ cm^{-1}), the ionized orbital is expected to be slightly antibonding.

As shown in Table VIII, the energies of the molecular orbitals as calculated by the CNDO/2 method are in fair agreement with the experimental ionization potentials, where the sharp peak observed at 12.79 eV is attributed to the loss of the 3p nonbonding electron on Cl. The molecular orbital sequence for Cl_2O is given as a_2^2, a_1^2, b_2^2, b_1^2.

E. Ultraviolet and Visible Spectroscopy

Two independent investigations[41,77] of the absorption spec-

TABLE VIII. Vertical Ionization Potentials (IP) of Cl_2O

Exptl IP, eV	Calcd IP (MO), eV	MO
11.02	9.0	b_2
12.37	10.4	b_1
12.65	10.7	a_2
12.79	12.5	a_1
15.90	17.0	b_2
16.65	18.1	a_1
17.68	20.3	b_1
20.64		

trum, in the ultraviolet and visible range, of gaseous Cl_2O over a large range of pressure (10–600 mmHg) have given results in very good agreement. The absorption begins at 660 nm and is continuous over the entire range, with maxima of increasing intensities at 630, 530, 410, and 255 nm. Initiation of the continuum is attributed to the process in eq 31, but the reaction in eq 32 may also be important.[78] The minimum energies for the occurrence of reactions 31 and 32 have been calculated as 36.5 kcal/mol (784 nm) and 41 kcal/mol (698 nm), respectively. The absorption at 256 nm (112 kcal/mol) may be due to the dissociation shown in eq 33, which requires 99 kcal/mol.[41]

$$Cl_2O + h\nu \rightarrow Cl + ClO \qquad (31)$$

$$Cl_2O + h\nu \rightarrow Cl_2 + O \qquad (32)$$

$$Cl_2O + h\nu \rightarrow Cl + Cl + O \qquad (33)$$

Conflicting results have been published[32,79] on the ultraviolet absorption spectra of Cl_2O in carbon tetrachloride solution. In what appears to be the least reliable study, three maxima were reported: 320, 395, and 415 nm. The first, at 320 nm, was attributed to the presence of Cl_2 in the unpurified sample. Indeed, the relative height of that peak suggests that chlorine was the main species present in solution, possibly because of a low conversion ratio in the preparation. Since the true spectrum of small concentrations of Cl_2O may well be masked by the broad absorption of chlorine, the assignment of the other two peaks, 345 and 415 nm, to Cl_2O is doubtful.

Indeed, those peaks have not been recorded by more careful workers who used purified Cl_2O in their study.[79] The latter investigators reported a strong sharp band at 264 nm, with a possible shoulder at 310 nm. This spectrum is quite distinct from that of Cl_2 in CCl_4 which exhibits a large maximum at 220 nm and a smaller one at 330 nm.[79,80] To confirm that Cl_2O was the species responsible for the absorption at 264 nm, anhydrous acetic acid was added to the CCl_4 solution; the formation of water was observed, and a change in the spectrum to that of acetyl hypochlorite (eq 34).

$$Cl_2O + 2HOAc \rightarrow 2ClOAc + H_2O \qquad (34)$$

In confirmation of the second[79] of the two studies just described, the spectrum of Cl_2O in trichlorotrifluoroethane was found to exhibit a broad maximum centered around 260 nm.[81]

F. Infrared Spectroscopy

The assignment of the three fundamental vibrations in the infrared spectrum of chlorine monoxide (Table IX) was a matter

TABLE IX. Infrared Spectra of Cl_2O

Authors	Bailey and Cassie	Bailey and Cassie	Hettner, Pohlman and Schumacher	Penney and Sutherland	Hedberg	Andrews and Raymond	Rochkind and Pimentel					
Reference	82	83	84	85, 86	87	88	53					
Phase	Gas	Gas	Gas	Gas	Gas	Argon matrix	Argon matrix	N_2 matrix	Gas	Solid	Symmetry	Contour
Vibration	Observed wave numbers, cm^{-1}											
ν_1	639	1233 1260	680	684[a] 680[a]	688	639.7 637.0 634.6	638.6 635.6	639.9 637.0	(640)	630.7	A_1	$\perp$
ν_2	973	628 651	330		(320)				300	296.4	A_1	$\perp$
ν_3	1245	969 973 980	973	973	969	677.6 675.6 673.8			677.2 685.9 691.8	671.8 669.8 667.8	B_1	$\parallel$
$\nu_3 - \nu_2$									366 379 389		B_1	Hybrid (?)
$\nu_1 + \nu_3$				1245					1310 1320 1326	1331.6 1327.7 1322.7	B_1	$\parallel$ (?)
$\nu_2 + \nu_3$						965.5 960.0			967.2 971.9 977.1	971.4 965.7 960.4	B_1	Hybrid
$2\nu_1$	1305			1331								
$2\nu_2$		1311[b]		684[a] 680[a]								
$2\nu_3$									(1360)	1331.6 1327.7 1322.7	A_1	$\perp$
$3\nu_3$									1935 1945 1952	1979.4 1973.3	B_1	$\parallel$ (?)

[a] ν_1 or $2\nu_2$. [b] Tentative assignment by original authors.

TABLE X. Fundamental Vibration Frequencies for the Cl_2O Molecule

Frequencies in wave numbers, cm^{-1}			Spectroscopic method	Ref
ν_1	ν_2	ν_3		
630.7	296.4	670.8	Infrared	53
634	293	673	Raman	91
619.2 ± 5	292.5 ± 1	705 ± 12	Microwave	74

TABLE XI. Force Constants Calculated for the Cl_2O Molecule

Source of spectroscopic data	Infrared[53]	Microwave[74]	Electron diffraction[92]
f_d, mdyn/Å	2.75 ± 0.02	2.882 ± 0.078	2.75
f_{dd}, mdyn/Å	0.40 ± 0.01	0.308 ± 0.048	0.40
$f_{d\alpha} \times 10^3$, dyn/rad	0.13 ± 0.01	0.283 ± 0.020	0.26
$f_\alpha \times 10^3$, erg/rad^2	1.32 ± 0.02	1.223 ± 0.006	1.32

of controversy among early investigators in the field.[82-88] However, the results of electron diffraction and microwave spectroscopy have latterly been available to establish that Cl_2O is a nonlinear molecule of point group C_{2v}. The rotational constants found by microwave spectroscopy are $A = 42\,044$, $B = 3682$, and $C = 3380$ MHz.[89,90] Thus $A > B \approx C$, and the species Cl_2O is a near-prolate symmetric top. In this approximation, the ν_3 vibration of Cl_2O (symmetry B_1) will display parallel rotational structure, while the vibrations ν_1 and ν_2 (symmetry A_1) will exhibit a perpendicular rotational structure.

By considering the contours of the absorption bands, comparing experimental spacings of the rotational components with those calculated from the moments of inertia, and comparing observed and calculated isotopic shifts (both oxygen and chlorine), Rochkind and Pimentel[53] established the unambiguous vibration assignments shown in Table IX. Polarized Raman spectroscopy[91] and microwave spectroscopy[74] have subsequently provided confirmation of the assignments (Table X).

Table XI summarizes the force constants of Cl_2O, expressed in terms of the internal valence coordinates system, and calculated from fundamental vibration frequencies (Table X) by the general harmonic potential function (eq 35) in the valence force field approximation (GVFF).

$$2V = f_d(\Delta d_1{}^2 + \Delta d_2{}^2) + f_\alpha(\Delta\alpha)^2 + 2f_{d\alpha}(\Delta d_1 + \Delta d_2)\Delta\alpha + 2f_{dd}\Delta d_1\Delta d_2 \quad (35)$$

Although computed from two independent sources of experimental data, infrared[53] and microwave[74] spectroscopy, the principal force constants, f_α and f_d, are in good agreement. The originally discordant results[53,74] for the cross-term $f_{d\alpha}$ were subsequently resolved by analysis of the force field derivation from vibrational frequencies;[92] the value of 0.13×10^{-3} dyn/rad proved to be in error and was corrected to 0.26×10^{-3} dyn/rad, in good agreement with the 0.283×10^{-3} dyn/rad computed from microwave data. The disagreement between the two values found for f_{dd} was not considered too significant[74] since the elements of the force constant matrix, $F_{11} = f_d + f_{dd}$ and $F_{33} = f_d - f_{dd}$, which are more closely related to the experimental data in both methods, are in good agreement: $F_{11} = 3.19$ and 3.15×10^5, and $F_{33} = 2.57$ and 2.35×10^5 dyn/cm.

It is of interest to note here a previously proposed[93] empirical relationship, eq 36, between the Cl–O stretching frequency and the corresponding bond length. If 1.70 Å is taken as the length of the Cl–O bond (see section V.C), then the equation gives a stretching force constant of 3.39×10^5 dyn/cm, in relatively good agreement, considering the crudeness of the method, with the $2.75–2.80 \times 10^5$ dyn/cm shown in Table XI.

$$\log k_{Cl\text{-}O} = -6.45 \log r_{ClO} + 7.0 \quad (36)$$

TABLE XII. Raman Spectrum of Liquid Cl_2O[91]

Infrared frequencies, cm^{-1}	Raman frequencies, cm^{-1}	Depolarization ratio	Symmetry	Vibration
630.7	634	0.25	A_1	ν_1
296.4	293	0.42	A_1	ν_2
670.8	673	0.77	B_1	ν_3

TABLE XIII. Raman Spectrum of Solid Chlorine Monoxide at 77 K[91]

Vibration	Frequencies, cm^{-1}	Symmetry
ν_2	301.1; 303.1	A_1
ν_1	625.3; 627; 628.3; 636.1	A_1
ν_3	668.5; 669.4; 670.7; 671.3	B_1
$\nu_3 + \nu_2$	938.7; 941.2; 945.7	B_1
$\nu_1 + \nu_3$	1308	B_1
$2\nu_3$	1321.3; 1327.1; 1330.3	A_1

The work of Rochkind and Pimentel[53] rendered obsolete all previously published[52,85-87,94-97] force constants of Cl_2O calculated from its vibration frequencies. Nevertheless, the calculations themselves remain of interest for having been concerned with improving and comparing computational procedures, mainly in the valence force-field approximation, but also in the Urey–Bradley force field approximation.[52,95]

The results in Table XI, from the GVFF approximation, now seem to constitute a standard against which are compared the various other approximation methods for the computation of force constants.[98-101] However, further discussion of these computations, even where they include chlorine monoxide as examples of XY_2 molecules, is beyond the scope of this review.

G. Raman Spectroscopy

The assignment of the fundamental infrared vibration frequencies[53] has been confirmed by polarization studies of the Raman spectrum[91] of liquid Cl_2O (Table XII). The spectrum of solid Cl_2O (77 K) is more complex, each fundamental being split by the crystal field into two or three components (Table XIII).

The Raman spectrum of Cl_2O isolated in an argon matrix[102] exhibits three bands, at 638, 298, and 678 cm^{-1}, in good agreement with the values shown in Table XII for infrared vibration bands and the Raman bands of the liquid.

H. Microwave Spectroscopy

Complete analyses[74,89,90] of the microwave spectra of the three species $^{35}Cl_2O$, $^{37}ClO^{35}Cl$, and $^{37}Cl_2O$, have yielded the rotational constants, A, B, and C, and the centrifugal distortion constants of the chlorine monoxide molecule. The rotational constants were used to calculate the effective moments of inertia, I_A, I_B, and I_C, which were, in turn, used for the computation of interatomic distances and bond angle. The results are summarized in Table VII. They agree well with results from electron diffraction studies.

The centrifugal distortion constants are functions of the harmonic force constants and have been used, in their inverse relationship, to compute the corresponding vibration frequencies (Tables X and XI). The latter have provided good confirmation of the results of infrared spectroscopy.

I. The Cl–O Bond in Cl_2O

Analysis[89] of the nuclear quadrupole coupling coefficient has shown that the asymmetry about the Cl–O bond is in the direction corresponding to the loss of an electron from the chlorine p orbital, which is perpendicular to the plane of the molecule. The strongly negative coupling constant in this direction has suggested that each of the structures Cl^+O^-Cl makes at least a 25% contribution to the ionicity of the molecule. Computation from an empirical formula[103] which relates percent ionicity to the electronegativity difference of the bonded atoms gives ionic character as 14%.

However, there is considerable contrary evidence that the Cl–O bond in Cl_2O has little or no ionic character. Thus, for example, a low value was found[53] for the force constant, f_d—the lowest in the series Cl_2O, ClO_2^-, ClO_3^-, ClO_4^-. Furthermore, the bond length of 1.70 Å (among the highest recorded for a Cl–O bond) has often been taken to indicate that Cl_2O provides the prototype of the single covalent Cl–O bond. It is interesting to note that if the currently accepted stretching constant, $k_{ClO} = 2.75 \times 10^5$ dyn/cm, is inserted into the empirical relationship[93] (eq 37) derived for Cl–O, Si–O, S–O, and P–O bonds, the bond order of Cl–O in Cl_2O works out to 0.95, in good agreement with the concept of a single bond.

$$N_{Cl-O} = 1.02 \times 10^{-6} k_{Cl-O} + 0.66 \qquad (37)$$

Additional support for the notion that Cl–O is a single covalent bond comes from semiempirical quantum chemical calculations. An internally consistent LCAO-MO method, based on Moffit's "atoms in molecules" method, but with somewhat different parameters, predicts a pure σ bond with no polar π-electron character.[104] The two-center exchange integral $[\beta(\pi)]$ is linearly correlated with the Cl–O distance and with the stretching force constants in the series Cl_2O, ClO_2^-, ClO_3^-, ClO_4^-, ClO_2. The "extended-Hückel" LCAO-MO approximation also gives a zero π population; it estimates the energy of atomization as 101.2 kcal/mol as compared with an experimental value of 103.0 kcal/mol.[105] By the CNDO/2 approximation, it has been found that there is a very small ($\approx$1%) participation of d orbitals in the molecular orbitals of Cl_2O.[76] The energy levels and the symmetries of the molecular orbitals are shown in Table VIII.

VI. Chemical Properties

A. Photochemistry

1. Photochemical Stability

Various observations of the stability of Cl_2O in the presence of light seem to disagree, probably because of differences in the initial purity of the samples being studied. In any event, some level of shielding from intense light sources would seem to be a desirable precaution when working with this substance.

Balard himself[1] had noted that diffuse daylight did not decompose Cl_2O; exposure to bright sunlight, however, did cause decomposition within a few minutes, but there was no detonation. Later investigators in the 19th century[35] said that the gas did not suffer appreciable decomposition during a 15-min exposure to the direct rays of the sun.

One group of investigators in the 1930's[47] observed that Cl_2O tended to explosive behavior in the presence of strong light. They were challenged by another group[106] who claimed that a light of 500 candle power, placed 2.5 cm from the wall of a spherical vessel, 7.6 cm in diameter, containing Cl_2O at a pressure of 0.5 atm, did not trigger an explosion.

The literature does not appear to contain any other observations on this topic that are either more recent or more systematic.

2. Photolysis of Gaseous Chlorine Monoxide

In one of the earliest studies of the photolysis of chlorine monoxide, which decomposes principally to Cl_2 and O_2, chlorine dioxide was identified as a minor product.[12] Of particular concern, however, was the influence of chlorine, almost always present initially as an impurity, on the course of the reaction. It was soon found that the rate of photolytic decomposition of Cl_2O was independent of the partial pressure of the free chlorine in the gas[12,41,107,108] and proportional to the total amount of energy absorbed,[12,107] whether absorbed by Cl_2O itself or by Cl_2. Thus, photochemical decomposition is sensitized by Cl_2.

A mechanism was proposed in 1929[109] to account for the quantum yield of approximately 2 which had been obtained from investigations using violet light in the range of 410–470 nm.[12,107] It was suggested that ClO was a significant intermediate in the reaction. Only the initiation step would be affected by the presence of chlorine, the unsensitized initiation being described by eq 38 and the chlorine-sensitized initiation by eq 39. The propagation (eq 40) and termination (eq 41) reactions would be the same, whether the initiation was sensitized or not.

$$Cl_2O + h\nu \rightarrow ClO + Cl \qquad (38)$$

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (39)$$

$$Cl + Cl_2O \rightarrow ClO + Cl_2\ (+14\ \text{kcal/mol}) \qquad (40)$$

$$ClO + ClO \rightarrow Cl_2 + O_2\ (+74\ \text{kcal/mol}) \qquad (41)$$

Subsequent studies of the visible and ultraviolet absorption spectra of chlorine monoxide revealed that absorption begins at 660 nm and is continuous through the entire ultraviolet region, with maxima at 630, 530, 410, and 256 nm.[41,77] Accordingly, the kinetics of photodecomposition was reinvestigated at 436, 365, and 312 nm[41] and at 235–275 nm.[108] At 365 nm, the average quantum yield was 3.5, and the 10° temperature coefficient, which was 1.09 at 10 °C, increased to 1.1 at 25 °C, and continued to rise as the temperature was increased.[41] The formation of a higher oxide of chlorine, in addition to ClO_2, was observed. At the shorter wavelengths, the quantum yield was 4.5, and the presence of oxygen or ozone had no influence on the rate of decomposition.[108] The mechanism advanced[41] to account for these observations, and shown in Table XIV, contains additional initiation, and propagation steps, of which reactions 45 and 40a are certainly infrequent, and reactions 40 and 44 would represent the principal paths of chain propagation. The quantum yield suggests short chains, and hence several termination reactions.

The photodecomposition of Cl_2O at 564 nm has been found to be sensitized by bromine, with a quantum yield of 4.3 at 19 °C.[110] The process involves short chains and is accompanied by an appreciable dark reaction. The similar quantum yields, virtually equal within experimental error, of the sensitized and unsensitized reactions suggest that energy exchange between Br_2 and Cl_2O is very specific and takes place at nearly every collision. The same efficiency has been observed for the bromine-sensitized photodecomposition of ClO_2[111] and was interpreted as an example of the ability of molecules with permanent dipoles to be efficient deactivators of molecules activated by light.[112] The mechanism in Table XIV was adapted to explain

TABLE XIV. Mechanism of Photolysis of Cl_2O[41]

Initiation:		
$Cl_2O + h\nu \rightarrow Cl + Cl + O$	($\lambda < 306$ nm)	(42)[a]
$Cl_2O + h\nu \rightarrow ClO + Cl$	($\lambda < 630$ nm)	(38)
$Cl_2 + h\nu \rightarrow 2Cl$		(39)
Propagation:		
$Cl + Cl_2O \rightarrow Cl_2 + ClO$	(+14 kcal/mol)	(40)
$ClO + Cl_2O \rightarrow ClO_2 + Cl_2$	(+30 kcal/mol)	(43)
$ClO + Cl_2O \rightarrow Cl_2 + O_2 + Cl$	(+31.5 kcal/mol)	(44)
$ClO + Cl_2O \rightarrow 2ClO + Cl$	(−43 kcal/mol)	(45)
$Cl_2 + ClO \rightarrow Cl + Cl_2O$	(−14 kcal/mol)	(40a)
Termination:		
$Cl + Cl + M \rightarrow Cl_2$		(46)
$ClO + ClO \rightarrow Cl_2 + O_2$	(+74 kcal/mol)	(41)
$Cl + ClO + M \rightarrow Cl_2O$		(47)
$Cl + ClO_2 \rightarrow Cl_2 + O_2$		(48)

[a] Equation numbers in parentheses.

TABLE XV. Mechanism of Cl_2O Photolysis (λ >306 nm)

Step	Reaction	Rate constant, l. mol^{-1} s^{-1}	Eq no.
Initiation	$Cl_2O + h\nu \rightarrow Cl + ClO$ (unsensitized)		38
	$Cl_2 + h\nu \rightarrow 2Cl$ (sensitized)		39
Propagation	$Cl + Cl_2O \rightarrow Cl_2 + ClO$	$k_{40} > 4 \times 10^8$	40
	$ClO + Cl_2O \rightarrow Cl + Cl_2 + O_2$	$k_{44} = 5.3 \times 10^4$	44
	$Cl_2O + ClO_2 \rightarrow Cl_2 + O_2 + ClO$	$k_{51} \simeq 10^5$	51
Termination	$ClO + ClO \rightarrow Cl_2 + O_2$	$k_{41} = 2.4 \pm 0.4 \times 10^7$	41
	$ClO + Cl_2O \rightarrow ClO_2 + Cl_2$	$k_{48} \simeq 10^7$	43

TABLE XVI. Mechanism of Cl_2O Photolysis[114] (λ >310 nm)

Step	Reaction	Rate constant, l. mol^{-1} s^{-1}		Eq no.
		Ref 114	Ref 113	
Initiation	$Cl_2O + h\nu \rightarrow ClO + Cl$			38
	$Cl_2 + h\nu \rightarrow 2Cl$			39
	$Br_2 + h\nu \rightarrow 2Br$			53
Propagation	$Cl + Cl_2O \rightarrow ClO + Cl_2$	$k_{40} = 4.1 \times 10^8$	$k_{40} > 4 \times 10^8$	40
	$Br + Cl_2O \rightarrow ClO + ClBr$	$k_{54} = 6.1 \times 10^8$		54
	$ClO + Cl_2O \rightarrow Cl + Cl_2 + O_2$	$k_{44} = 6.5 \times 10^5$	$k_{44} = 5.3 \times 10^4$	44
	$Cl + ClO_2 \rightarrow 2ClO$			52
	$ClO + Cl_2O \rightarrow ClO_2 + Cl_2$	$k_{43} = 2.6 \times 10^5$	$k_{43} \simeq 10^5$	43
Termination	$2ClO \rightarrow Cl_2 + O_2$	$k_{41} = 2.8 \times 10^7$	$k_{41} = 2.4 \times 10^7$	41

TABLE XVII. Mechanism of Cl_2O Photolysis[114] (λ <280 nm)

Step	Reaction	Rate constant, l. mol^{-1} s^{-1}	Eq no.
Initiation	$Cl_2O + h\nu \rightarrow 2Cl + O$		42
	$Cl_2O + h\nu \rightarrow Cl_2 + O$		55
Propagation	$Cl + Cl_2O \rightarrow ClO + Cl_2$	$k_{40} = 4.1 \times 10^8$	40
	$O + ClO \rightarrow Cl + O_2^* \ (v'' \leq 14)$	$k_{56} = 7.5 \times 10^3$	56
	$ClO + h\nu \rightarrow Cl + O$		57
Relaxation	$O_2^* \ (v'' = 12) + Cl_2O \rightarrow O_2^* \ (v'' \leq 12) + Cl_2O$	$k_{58} = 1 \times 10^8$	58
	$O_2^* \ (v'' = 12) + Cl \rightarrow O_2^* \ (v'' \leq 12) + Cl$	$k_{59} = 2 \times 10^9$	59
	$O_2^* \ (v'' = 12) + ClO \rightarrow O_2^* \ (v'' \leq 12) + ClO$	$k_{60} = 2 \times 10^8$	60

sensitization by bromine, reaction 39 being replaced by reactions 49 and 50.

$$Br_2 + h\nu \rightarrow Br_2^* \qquad (49)$$

$$Br_2^* + Cl_2O \rightarrow Br_2 + Cl + ClO \qquad (50)$$

In the presence of hydrogen, the photolysis of Cl_2O gives H_2, O_2, and Cl_2 as the main products, but small amounts of HCl and H_2O are also found.[106] Acceleration of the photodecomposition can occur to the point where the production of HCl becomes predominant. The chain propagators are thought to be ClO radicals, and not H radicals.

Experiments with flash photolysis[113] have tended to support the mechanism in Table XIV. The flash photolysis of Cl_2O in a large excess of an inert gas (O_2, N_2, CO_2, SF_6) can conveniently be divided into three stages. During the flash (100 μs), the concentration of Cl_2O falls sharply, while [ClO] reaches a maximum. In the 10 ms following the flash, [ClO] decreases rapidly, while [Cl_2O] falls only slowly. At the end of 10 ms, ClO_2 begins to appear; its concentration builds up rapidly in the first seconds, then more slowly, reaches a maximum at 30 s, and then slowly decays. From the decay of Cl_2O and the ClO radical, the rate of formation of ClO_2, and other data available in the literature, the mechanistic details shown in Table XV were worked out.[113] All but one of these reactions (eq 51) are in the previously presented mechanism.[41]

$$Cl_2O + ClO_2 \rightarrow Cl_2 + O_2 + ClO \qquad (51)$$

By combining k_{40}, k_{41}, k_{43}, and the quantum yield of 3.5,[41] k_{44} was computed as 2×10^4 l. mol^{-1} s^{-1}, which, considering the possible sources of error, was in reasonable agreement with the experimental value of 5.3×10^4.

However, the interpretation represented by Table XV is limited because it carries the assumptions that the propagation reaction 52 and the termination step 48 do not occur, and that the decay of ClO_2 occurs via reaction 51. More recent experimental evidence[114] suggests that reaction 51 is not present, and that reaction 52 is much faster than reaction 48. Flash photolysis of Cl_2O, both unsensitized, and sensitized by Cl_2 and Br_2, at a wavelength greater than 310 nm led to proposal of the mechanism in Table XVI. An average quantum yield of 4.9 ± 1, redetermined under flash photolysis conditions, agrees well with the value of 4.0 calculated from the rate constants in the table.

$$Cl + ClO_2 \rightarrow 2ClO \qquad (52)$$

In flash photolysis at λ <280 nm, vibrationally excited oxygen, O_2^*, was observed. Its concentration increased with increasing pressure of Cl_2O and energy of the flash, and was higher in a quartz than in a glass vessel.[114] The mechanism in Table XVII was suggested. As indicated by the constants, the rate of relaxation would be determined essentially by the concentration of chlorine atoms in the reaction.

3. Photolysis of Cl_2O in Carbon Tetrachloride Solution

Compared to gas-phase photolysis, scant attention has been paid to the photolysis of chlorine monoxide in CCl_4 solution, and only two investigations have been reported,[21,22] each giving a different quantum yield. The difference may be explicable by the observation that the course of photolysis is strongly influenced by the purity of the solvent.[22]

In the first of the two investigations[21] a quantum yield close to 1 was obtained by photolysis in violet light (410–470 nm). In the second investigation,[22] the yield was found to be at least 1.8 molecules of Cl_2O decomposed per quantum absorbed. Significant quantities of chlorine dioxide were formed in this reaction, with an initial rate estimated as 0.35 mol/quantum.

No mechanisms have been proposed for these photolyses, and there is no report of any experiment performed at 264 nm, the absorption maximum of Cl_2O in CCl_4 (see section V.E).

4. Photolysis of Matrix-Isolated Cl_2O

Chlorine monoxide has been photolyzed while suspended in matrices of solid nitrogen or argon, with the formation of products observed by means of infrared spectroscopy.[115,116] It was concluded that five products were formed: three chlorine-containing products, ozone, and (in the N_2 matrix) N_2O. Analysis of chlorine and oxygen isotopic shifts suggested that the three chlorine-containing products are $Cl\cdots Cl\overline{\cdots}O$ and two dimers, $(ClO)_2$, of different isomeric structures. The mechanism of the photolysis is rationalized as in eq 61–75. $Cl\cdots Cl\overline{\cdots}O$ is formed through recombination (eq 69) within the matrix cage. One of the $(ClO)_2$ dimers can be formed through the photolysis of Cl_2O pairs (eq 70–72), because of incomplete isolation in the matrix.

$$Cl_2O + h\nu \rightarrow ClO\,(^2\Pi) + Cl\,(^3P) \quad \lambda < 817\text{ nm} \qquad (61)$$

$$Cl_2O + h\nu \rightarrow Cl_2\,(^1\Sigma) + O\,(^1D) \quad \lambda < 331\text{ nm} \qquad (62)$$

$$ClO\,(^2\Pi) + h\nu \rightarrow Cl\,(^2P) + O\,(^3P) \quad \lambda < 281\text{ nm} \qquad (63)$$

$$ClO\,(^2\Pi) + h\nu \rightarrow Cl\,(^2P) + O\,(^1D) \quad \lambda < 263\text{ nm} \qquad (64)$$

$$ClO_2 + h\nu \rightarrow Cl_2 + O_2 \qquad (65)$$

$$(ClO)_2 + h\nu \rightarrow Cl_2O + O \qquad (66)$$

$$Cl\cdots Cl\overline{\cdots}O + h\nu \rightarrow Cl_2O \qquad (67)$$

$$Cl\cdots Cl\overline{\cdots}O + h\nu \rightarrow Cl_2\,(^1\Sigma) + O \qquad (68)$$

$$Cl + ClO \rightarrow Cl\cdots Cl\overline{\cdots}O \qquad (69)$$

$$Cl_2O + h\nu \rightarrow Cl + ClO \qquad (70)$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \qquad (71)$$

$$ClO + ClO \rightarrow (ClO)_2 \qquad (72)$$

Ozone and the second dimer, which are formed simultaneously, arise from the mechanisms in eq 73 and 74, respectively. Nitrous oxide comes from the reaction in eq 75.

$$O_2\,(^3\Sigma) + O\,(^3P) \rightarrow O_3\,(^1A) \qquad (73)$$

$$O\,(^3P) + Cl_2O \rightarrow (ClO)_2 \qquad (74)$$

$$N_2\,(^1\Sigma) + O\,(^1D) \rightarrow N_2O\,(^1\Sigma) \qquad (75)$$

Raman spectra[102] of the species obtained by laser photolysis (488 nm) of Cl_2O isolated in an argon matrix have confirmed the formation of the photoisomerism product $Cl\cdots Cl\overline{\cdots}O$. The latter gave strong bands at 962, 373, and 241 cm^{-1}, while a dimer, $(ClO)_2$, gave a band at 850 cm^{-1}. When the Cl_2O was photolyzed in an ozone matrix another dimer, $(ClO)_2$, was found; it gave an intense doublet at 995 and 986 cm^{-1}. The photoisomer of Cl_2O would have formed by eq 69, and the two dimers by eq 72 and 74, respectively.

B. Thermochemistry

1. Mechanism of Thermal Decomposition

The thermal decomposition of Cl_2O, which, like photolysis, yields primarily Cl_2 and O_2, was at first said to be homogeneous, its rate being unchanged when the reactive surface provided by the containing vessel was greatly augmented by the addition of glass wool.[117] However, evidence for a wall effect was later found,[118–120] so that the reaction is indeed heterogeneous. The decomposition begins after an induction period whose length is inversely proportional to the initial concentration of Cl_2O, while the initial velocity of decomposition depends upon the purity of the material, the dimensions of the container, and the temperature.[121] An increase observed[117] in the velocity of the reaction as it proceeds might be attributed to autocatalysis by either the Cl_2 or O_2 formed, except that the presence of added Cl_2, O_2, N_2, or air does not influence the course of the reaction.

At low temperatures (60–100 °C), the reaction is slow, reaching completion in 12 to 24 h. Above 100 °C, the rate increases so that at 150 °C, the reaction is complete within a few minutes.[117–121] At temperatures below 130 °C, the rate of decomposition of Cl_2O is proportional to its concentration,[117,118] while at 140 °C the rate is proportional to $[Cl_2O]^{0.75}$.[118] All reactions above 110 °C were found to end with an explosion.[118]

To account for all of these observations, two different mechanisms have been proposed. One interprets the shape of the pressure–time curves by postulating two consecutive bimolecular reactions, the first producing a pressure change less than that from the second,[117–122] with an unknown oxide of chlorine proposed as an intermediate. Since the individual stages of the reaction are not clearly defined, it is suggested that both stages must have similar rate constants, on the one hand, and activation energies, on the other. The activation energy, $E = 21$ kcal/mol, calculated from the slope of an experimentally determined Arrhenius plot, was found in good agreement with the values computed by applying collision theory of gas reactions,[123,124] or Eyring's empirical rule (expressing activation energy of a homogeneous bimolecular gas reaction as a function of both the heat of dissociation and the heat of reaction).[125] In the Damianovitch relationship dealing with the activation energies of isokinetic reactions, the activation energy of the thermal decomposition of Cl_2O has been found to correlate well with the activation energies of the decomposition of N_2O and HI.[126]

The other mechanism proposed to account for the observed data is a chain reaction, in which Cl atoms and ClO radicals are the chain carriers,[118–121,127] and adequately explains the explosion occurring at the end of the decomposition, the wall effect, and the acceleration that takes place as the reaction proceeds. On the negative side is the observation that diluent gases, such as Cl_2, O_2, N_2, or air, which could be expected to interfer with a chain reaction, actually had a negligible effect. Nevertheless, relatively recent evidence supports the chain mechanism, since ClO has been observed in the mass spectrum of products from the pyrolysis of Cl_2O at 350 °C,[65] and in the emission spectrum of Cl_2O subjected to shock-wave treatment.[128]

One chain mechanism has been proposed[129] on the basis of similarities between the behavior of the rate of decomposition of Cl_2O and of the rate of oxidation of ethane by oxygen. It has also been proposed that "nascent oxygen" could act as an autocatalyst in the thermolysis of Cl_2O.[130] However, the most favored mechanism is that illustrated in eq 76 to 83.[118] At temperatures below 130°, initiation occurs according to eq 76 and 77, but above 140°, when the order of reaction changes, reaction 78 becomes operative. In accordance with the chain-reaction mechanism, mathematical expressions, approximately fitting the experimental curves, have been derived[121,127] for the rate of decomposition of Cl_2O.

Initiation:

$$T \leq 130\text{ °C} \quad Cl_2O + Cl_2O \rightarrow ClO_2 + Cl + Cl_2 \qquad (76)$$

$$Cl + Cl_2O \rightarrow ClO + Cl_2 \qquad (77)$$

$$T > 140\text{ °C} \quad Cl_2O + Cl_2O \rightarrow 2ClO + Cl_2 \qquad (78)$$

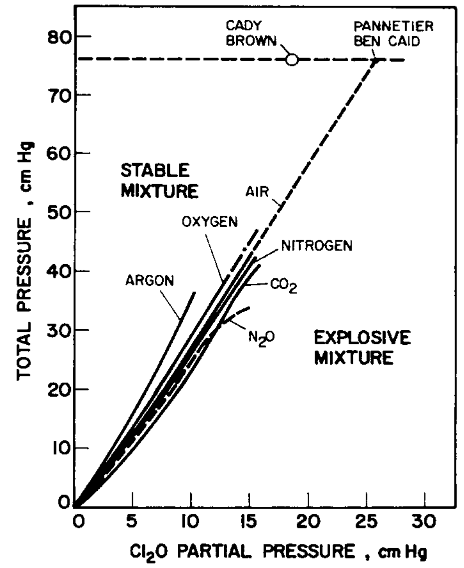


Figure 7. Explosive limit for chlorine monoxide in the presence of diluent gas.

Propagation:

$$ClO + Cl_2O \rightarrow ClO_2 + Cl_2 \quad (79)$$

$$ClO_2 \rightarrow ClO + O \quad (80)$$

$$ClO_2 \rightarrow Cl + O_2 \quad (81)$$

$$Cl_2O + O \rightarrow 2ClO \quad (82)$$

Termination:

$$ClO + ClO \rightarrow Cl_2 + O_2 \quad (83)$$

2. Explosive Decomposition

The question of whether Cl_2O was so unstable as to explode spontaneously was the subject of controversy among those who did the early research on this substance. Reports of extreme instability[3,33,34] were later denied;[35] the observed instability was attributed to the presence of organic impurities. Nonetheless, chlorine monoxide should itself be regarded as an explosive substance, since its detonation can be easily triggered by an electric spark, heating above 120 °C, or a rapid rate of heating at lower temperatures. The liquid is said to be particularly shock-sensitive, explosions having been encountered during the purification of gram quantities.[131] The quantity of energy liberated by the explosion of Cl_2O has been variously estimated as 21 735 ± 560 cal/mol,[47] 20 050 ± 1000 cal/mol,[48] and 25 100 ± 100 cal/mol.[49]

In mixtures of Cl_2O and oxygen (760 mmHg total pressure) at 23 °C, an electric spark induces an explosion when the concentration of Cl_2O exceeds 23.5%. Mixtures containing 25–30% Cl_2O explode weakly, with a yellow band moving up the tube. Concentrations of Cl_2O above 30% give violent explosions, with an orange-colored flash of light.[132] The pressure threshold for the spark-induced decomposition of pure Cl_2O was determined as 4.0 ± 0.1 mmHg.[133]

The presence of diluent gases tends to inhibit the explosion process. As shown in Figure 7, argon is the poorest inhibitor, while CO_2 is the best, for a partial pressure of Cl_2O below 12.5 mmHg. The anomalous behavior of N_2O is attributed to the formation of a molecular complex with Cl_2O.[133] The discrepancy, seen in Figure 7, between the experimental results of Cady and Brown[132] and the corresponding extrapolated value from the work of Pannetier and Ben Caid[133] can be explained by a possible contribution of light: Cady and Brown operated in "faint day light"; Pannetier and Ben Caid in complete darkness.

An empirical relationship has been established[134] which relates the temperature at the critical point of explosion to the partial pressure of Cl_2O. It is shown as eq 84, where P_m is expressed in mmHg, and T in K, $A = 2500$ and $B = -6.81$. A similar relationship can be derived from the collision theory of gas reactions, giving $A = 2250$, in good agreement with experiment.

$$\log (P_m/T) = (A/T) + B \quad (84)$$

C. Reactions with Inorganic Substances

1. Hydrogen Atoms

In his original investigation, Balard[1] found that no reaction occurred when Cl_2O and H_2 were mixed, but that the approach of a flame caused a violent explosion, which produced hydrochloric acid. The effect of hydrogen on the photolytic decomposition of Cl_2O (section VI.A.2) is to accelerate it and to cause the formation of HCl.[106] Under conditions where all the Cl_2 is not converted into HCl, small quantities of H_2O are also formed, in addition to the main products, which are Cl_2 and O_2. These reactions have not been investigated in detail, but the mechanism described by eq 85–88 has been proposed, where ClO is still the main chain carrier. No termination reactions were suggested.

$$Cl_2O + h\nu \rightarrow Cl + ClO \quad (85)$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \quad (86)$$

$$ClO + Cl_2O \rightarrow Cl_2 + O_2 + Cl \quad (87)$$

$$ClO + H_2 \rightarrow HCl + OH \quad (88)$$

In the reaction of Cl_2O with atomic hydrogen, the formation of products has been followed by mass spectrometry[135] and infrared chemiluminescence.[136,137] The reaction is complex. If H is in excess, HCl and H_2O predominate as major products with O_2 and Cl_2 appearing as only minor products. With Cl_2O in excess, after 100 msec, Cl_2 and O_2 are the main products, and smaller amounts of H_2O and HCl are detected. With an excess of Cl_2O, or an equimolar ratio, the formation of HOCl is observed, even at the shortest reaction time. Independent of the conditions used, 1.11 ± 0.1 mol of Cl_2O is consumed per atom of H. Molecular hydrogen is also consumed in smaller proportions. The primary step is conceived as a competition between reactions 89 and 90.

$$H + Cl_2O \rightarrow HOCl^{\dagger} + Cl \quad \Delta H = -63 \pm 3 \text{ kcal/mol} \quad (89)$$

$$H + Cl_2O \rightarrow HCl^{\dagger} + ClO \quad \Delta H = -68 \text{ kcal/mol} \quad (90)$$

In this reaction, HCl is produced with a distribution of vibrational energy that is markedly lower than its thermochemical limit. The seeming anomaly can be attributed, in part, to the energy required for the reorganization of the Cl–O bond from 1.70 Å in Cl_2O to 1.57 Å in ClO.[137]

Following pulsed electric discharges in a mixture of Cl_2O (0.5 mmHg) and H_2 (5 mmHg), a laser emission of 50–100 μs, with an output range of 3.6–4.0 μ was observed.[138] It was attributed to the chain reaction described by eq 89–94.

$$Cl + H_2 \rightarrow HCl + H \quad (91)$$

$$ClO + ClO \rightarrow 2Cl + O_2 \quad (92)$$

$$Cl + ClO + M \rightarrow Cl_2O + M \quad (93)$$

$$Cl + \text{wall} \rightarrow \tfrac{1}{2}Cl_2 + \text{wall} \quad (94)$$

2. Other Atoms

Just as in the reactions with H atoms, or with Cl atoms during pyrolysis, or during chlorine- and bromine-sensitized photolysis, the production of the radical ClO has been found to be the most important primary process in the reactions of Cl_2O with atoms of O, N, and alkali metals.

The reaction of Cl_2O with O atoms, in a fast-flow system at room temperature, has been monitored by mass spectrometry and appears to follow the scheme described by eq 95–99.[67]

$$O + Cl_2O \rightarrow 2ClO \quad k_{95} = 8.3 \times 10^9\ \mathrm{l.\ mol^{-1}\ s^{-1}} \qquad (95)$$

$$O + ClO \rightarrow O_2 + Cl \quad k_{96} > 6 \times 10^9\ \mathrm{l.\ mol^{-1}\ s^{-1}} \qquad (96)$$

$$Cl + Cl_2O \rightarrow Cl_2 + ClO \quad k_{97} > 4 \times 10^8\ \mathrm{l.\ mol^{-1}\ s^{-1}} \qquad (97)$$

$$Cl + \mathrm{wall} \rightarrow \tfrac{1}{2}Cl_2 \quad \text{slow with poisoned walls} \qquad (98)$$

$$2ClO \rightarrow Cl_2 + O_2 \quad k_{99} = 1.7 \times 10^7\ \mathrm{l.\ mol^{-1}\ s^{-1}} \qquad (99)$$

Under the same conditions, when Cl_2O was reacted with N atoms, 0.93 ± 0.1 mol of Cl_2O was decomposed per mole of atoms of nitrogen.[139] The presence of relatively long-lived ClO radicals was observed, but neither NO nor NCl was detected. The mechanism for the reaction with nitrogen atoms is summarized by eq 100–102 followed by reactions 95–99.

$$N + Cl_2O \rightarrow NCl + ClO \qquad (100)$$

$$k_{96} = (9.1 \pm 1.5) \times 10^8\ \mathrm{l.\ mol^{-1}\ s^{-1}}$$

$$N + NCl \rightarrow N_2 + Cl \quad k_{101} > 10^9\ \mathrm{l.\ mol^{-1}\ s^{-1}} \qquad (101)$$

$$N + ClO \rightarrow NCl + O \quad k_{102} > 10^9\ \mathrm{l.\ mol^{-1}\ s^{-1}} \qquad (102)$$

The matrix reaction of Cl_2O with alkali metal atoms at high dilution in argon leads to absorptions in the infrared region, which are attributed to the corresponding metal chloride, and to other absorption peaks attributed to ClO on the basis of frequency analysis, isotopic shift, and literature data.[88] The primary process can be described by eq 103, which can be considered to represent the most important process in the reaction of Cl_2O with atomic species, i.e., M = Li, Na, K, H, O, N, Cl, and Br.

$$M + Cl_2O \rightarrow MCl + ClO \qquad (103)$$

3. Alkaline and Alkali Earth Hydroxides

As the anhydride of hypochlorous acid, chlorine monoxide forms hypochlorites with alkaline and alkali earth metal hydroxides. By extracting a carbon tetrachloride solution of Cl_2O with an aqueous suspension or solution of $M(OH)_n$ (M = Li, Na, K, Sr, Ca, Ba), and evaporating the resulting extract in vacuo at 40– 50 °C, the pure hypochlorite, $M(ClO)_n$, or one of its crystalline hydrates, can be obtained.[140] Li, Ca, Ba, and Sr hypochlorites are stable. Sodium hypochlorite shows some tendency to decompose on drying, while the potassium salt is even less stable and, during drying, is oxidized to the peroxide by any excess of Cl_2O (eq 104).

$$2KOCl + Cl_2O \rightarrow K_2O_3 + 2Cl_2 \qquad (104)$$

Generally, the dry hypochlorites react with chlorine monoxide to form chlorates, according to eq 105.[141] The rate of chlorate formation decreases in the order Na > Ba > Sr > Li > Ca. After 8 h, the reaction is complete for NaOCl, but only 30% complete for $Sr(OCl)_2$.

$$M(ClO)_n + 4Cl_2O \rightarrow M(ClO_3)_n + 4Cl_2 \qquad (105)$$

The heat of reaction of Cl_2O in CCl_4 solution with aqueous hydroxyl ions (eq 106) was determined[142] calorimetrically at 5, 10, 25, and 35 °C to give the thermodynamic properties shown as eq 107 and 108. By comparing $\Delta G°_{298}$, computed according to eq 108 with data available in the literature, the integration constant was evaluated as $I = 1.8874$.

$$Cl_2O\ (CCl_4) + 2OH^-(aq) \rightarrow 2OCl^-(aq) + H_2O(l) \qquad (106)$$

$$\Delta H°_T = -80.86 + 0.3204T - 0.000420T^2 \qquad (107)$$

$$\Delta G°_T = -80.86 - 0.3204T \ln T + 0.000420T^2 + IT \qquad (108)$$

4. Alkaline Hydrogen Peroxide

The heat of reaction of chlorine monoxide with basic aqueous solutions of hydrogen peroxide (eq 109), as determined[63,143] calorimetrically at 5, 10, 25, and 35 °C, gave the thermodynamic functions in eq 110 and 111. By computation of $\Delta G°_{298}$ from the free energies of formation of $HO_2^-(aq)$, $H_2O(l)$, $Cl^-(aq)$, and $Cl_2O(CCl_4)$, it was found that $I = -0.1788$

$$Cl_2O(CCl_4) + 2HO_2^-(aq) \rightleftarrows 2Cl^-(aq) + H_2O(l) + 2O_2(g) \qquad (109)$$

$$\Delta H°_T = -70.50 - 0.2677T + 0.000740T^2 \qquad (110)$$

$$\Delta G°_T = -70.50 + 0.2677T \ln T - 0.000740T^2 + IT^2 \qquad (111)$$

5. Nitrogen Oxides

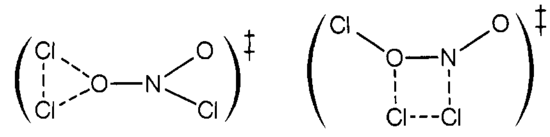
Table XVIII summarizes the reactions of chlorine monoxide with nitrogen dioxide and dinitrogen pentoxide in the gas phase, in solution in an inert solvent (1,1,2-trichloro-1,2,2-trifluoroethane), and in the melt.[81,144–148] Nitrosyl chloride (NO_3Cl) and nitryl chloride (NO_2Cl) have been identified as the main products.

The ratio of the rate constants at 20 °C, for the same reaction in the gas phase and in solution, has been discussed in terms of both the collision theory and the transition state theory of chemical kinetics.[147]

The activation energy (−7500 kcal/mol) and the Arrhenius factor (1.46×10^4 l. mol^{-1} sec^{-1}) for the reaction of chlorine monoxide with nitrosyl chloride in trichlorotrifluoroethane were both much lower than expected for a bimolecular reaction. Nevertheless, the values found were shown to be consistent with the reaction mechanism described by eq 112 and 113. Two structures, Ia and Ib, were proposed for the activated complex [$Cl_2O{\cdot}NOCl$] shown in these equations, but the available evidence did not permit any definite assignment.

$$Cl_2O + NOCl \overset{K_1}{\rightleftarrows} [Cl_2O{\cdot}NOCl] \qquad (112)$$

$$[Cl_2O{\cdot}NOCl] \xrightarrow{k_1} Cl_2 + NO_2Cl \qquad (113)$$



Ia Ib

The reaction of Cl_2O with NO_2 in the melt (−25 °C) was interpreted as proceeding in two steps, the first being the formation of N_2O_5, which, in the second, further reacts with Cl_2O to form NO_3Cl.[146,149] It has recently been proposed that the reaction of N_2O_5 with Cl_2O is a nitration by NO_2^+ ($N_2O_5(s) \equiv NO_2^+\ NO_3^-$) according to eq 114. This proposal was based on the observation that yields of NO_3Cl obtained by nitration of Cl_2O by various NO_2X compounds decreases in the order X = NO_3^- > BF_4^- > ClO_4^- = SO_3F^-. This order is the same as the order of ionicity of the NO_2–X bond.[150]

$$NO_2^+ + Cl_2O \rightarrow NO_3Cl + Cl^+ \qquad (114)$$

6. AsF$_5$ and SbF$_5$

Chlorine monoxide reacted with AsF_5 to give a complex at −78 °C, which, at about −50 °C, eliminated chlorine to yield what was first believed to be an odd-electron molecule, $ClOAsF_5$.[145] It was later proven that the product was, in fact, the ionic compound $ClO_2^+AsF_6^-$,[151,152] for which eq 115–118 give the postulated mechanism of formation.[152]

$$2Cl_2O + AsF_5 \rightarrow ClO_2^+AsF_5Cl^- + Cl_2 \qquad (115)$$

$$ClO_2^+AsF_5Cl^- + AsF_5 \rightarrow ClO_2^+AsF_6^- + AsF_4Cl \qquad (116)$$

TABLE XVIII. Reactions of Cl_2O with NO_2 and N_2O_5

Reactions	Rate equation	Phase	Frequency factor, l. mol^{-1} s^{-1}	Activation energy, kcal/mol	Ref
$Cl_2O + 2NO_2 \rightarrow NO_3Cl + NO_2Cl$	$-d[Cl_2O] = k[Cl_2O][NO_2]$	Gas	4.35×10^7	11.6	146
Mechanism $Cl_2O + NO \rightarrow NO_2Cl + ClO$ $NO_2 + ClO \rightarrow NO_3Cl$		Solution (Freon 113)	3.50×10^7	10.4	145
$2NO_2 + 2Cl_2O \rightarrow 2NO_3Cl + Cl_2$ Mechanism $2NO_2 + Cl_2O \rightarrow N_2O_5 + Cl_2$ $N_2O_5 + Cl_2O \rightarrow 2NO_3Cl$		Melt (−25 °C)			146 149
$2Cl_2O + 2N_2O_5 \rightarrow 2NO_3Cl + 2NO_2Cl + O_2$	$-d[Cl_2O]/dt = k[N_2O_5]$	Gas	3.6×10^{13}	24.6	147
Mechanism $2N_2O_5 \rightarrow 4NO_2 + O_2$ $NO_2 + Cl_2O \rightarrow NO_2Cl + ClO$ $NO_2 + ClO \rightarrow NO_3Cl$		Solution	4.0×10^{13}	24.5	145
$Cl_2O + N_2O_5 \rightarrow 2NO_3Cl$		Melt			146, 149
$Cl_2O + NOCl \rightarrow Cl_2 + NO_2Cl$		Gas			147
	$-d[NOCl]/dt = k[Cl_2O][NOCl]$	Solution (Freon 113)	1.46×10^4	7.5	147 148
$Cl_2O + NOCl \rightarrow O_2 + NO_2$		Melt			147

$$2AsF_4Cl \rightarrow AsF_5 + AsF_3Cl_2 \quad (117)$$

$$AsF_3Cl_2 + Cl_2O \rightarrow AsOF_3 + 2Cl_2 \quad (118)$$

The reaction of SbF_5 with Cl_2O is also complicated. The main products identified were ClO_2SbF_6, $SbOF_3$, Cl_2, and $ClO_2Sb_3F_{16}$.[153] Except for the last, the products formed are similar to those from AsF_5. Thus the reaction of SbF_5 with Cl_2O can proceed by a mechanism similar to that in eq 115–118. However, the reaction is not specific to Cl_2O, but general to all chlorine oxides; ClO_2SbF_6 and $SbOF_3$ are also formed when $SbISbF_5$ is reacted with ClO_2 and Cl_2O_6, and $ClO_2Sb_{13}F_{16}$ is also formed during the reaction of SbF_5 with ClO_2 and Cl_2O_7. Hence, a more general scheme is required to rationalize these observations.

7. Metallic and Metalloidic Halides

Metallic and metalloidic oxyhalides, which are often polymeric substances,[154–159] may be prepared by treating the corresponding halides with chlorine monoxide. In these reactions, 2 mol of chlorine is liberated for every mole of chlorine monoxide consumed. Reactions of this type are illustrated by eq 119–128. The reactions may be completed by the oxidation of the metal or metalloid to its highest oxidation state.

$$VOCl_3 + Cl_2O \rightarrow VO_2Cl + 2Cl_2 \quad (119)^{154}$$

$$P(NCl_2)_3 + 2Cl_2O \rightarrow PO_2Cl + 3NCl_3 \quad (120)^{155}$$

$$AsCl_3 + 2Cl_2O \rightarrow AsO_2Cl + 3Cl_2 \quad (121)^{155}$$

$$SbCl_5 + Cl_2O \rightarrow SbO_2Cl + 4Cl_2 \quad (122)^{155,158}$$

$$POCl_3 + MoCl_5 + Cl_2O \rightarrow MoO_2Cl_2{\cdot}POCl_3 + \tfrac{7}{2}Cl_2 \quad (123)^{159}$$

$$SnCl_4 + Cl_2O \rightarrow SnOCl_2 + 2Cl_2 \quad (124)^{156}$$

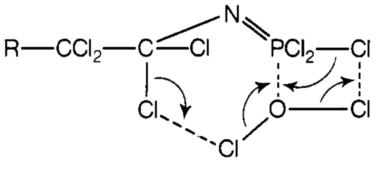
$$TiCl_4 + Cl_2O \rightarrow TiOCl_2 + 2Cl_2 \quad (125)^{157}$$

$$RCCl_2CCl_2N{=}PCl_3 + Cl_2O \rightarrow RCCl_2CCl{=}NPOCl_2 + 2Cl_2 \quad (126)^{160}$$

$$ArSO_2N{=}PCl_3 + Cl_2O \rightarrow ArSO_2Cl{=}NPOCl_2 + 2Cl_2 \quad (127)^{160}$$

$$PF_3Cl_2 + Cl_2O \rightarrow POF_3 + 2Cl_2 \quad (128)^{151}$$

The mechanism of these reactions is not known in detail, but a cyclic intermediate (eq 129) has been postulated[160] for the trichlorophosphate compounds (eq 126 and 127).



$$\xrightarrow{-2Cl_2} RCCl_2CCl{=}NPOCl_2 \quad (129)$$

The reaction of silver difluoride with Cl_2O at 65–70 °C has been reported as resembling the reactions of the chlorides.[15] However, since it is known that chlorine dioxide gives the same products on reaction with AgF_2, the mechanism in eq 130 and 131 has been proposed.

$$2Cl_2O \rightarrow ClO_2 + \tfrac{3}{2}Cl_2 \quad (50\ °C < t < 80\ °C) \quad (130)$$

$$ClO_2 + AgF_2 \rightarrow ClO_2F + AgF \quad (131)$$

8. Fluorine

The reaction of chlorine monoxide with fluorine has been investigated as a route for the preparation of chlorine trifluoride oxide, ClF_3O.[131] It was found that alkali metal fluorides catalyzed the reactions described by eq 132 and 133.

$$2F_2 + Cl_2O \rightarrow ClF_3O + ClF \quad (132)$$

$$3F_2 + Cl_2O \rightarrow ClF_3O + ClF_3 \quad (133)$$

High yields (40–80%) of ClF_3O were obtained by reacting fluorine with liquid Cl_2O, in the presence of alkali metal fluorides, at −78 °C for several days in a stainless steel vessel passivated with ClF_3. When no catalyst is used or when KF or NaF are present as catalyst, ClF is the main product. When CsF or RbF are the catalysts, ClF_3 is the favored product.

With a mixture of yellow mercuric oxide and chlorine, which is mainly Cl_2O absorbed in mercuric salts, the presence of fluorine produces only a small yield of $ClOF_3$, while ClF_3 and ClO_2F

are the main products. Gaseous fluorine, except when activated in a glow discharge, does not react with solid Cl_2O, but then it does give a low yield (1–2%) of ClF_3O.

That less than theoretical yield of ClF_3O is obtained in its synthesis from Cl_2O has been explained, at least in part, by a slow reaction which occurs between both compounds.[161] When an equimolar mixture of Cl_2O and ClF_3O was allowed to stand for 15 h at room temperature, only 88% of the starting compounds was recovered, and the presence of small quantities of ClF and ClO_2F was observed.

This result was explained by means of the reaction sequence 134–135, in which FClO is an unstable intermediate.

$$ClF_3O + Cl_2O \rightarrow 2[FClO] + ClF \qquad (134)$$

$$2[FClO] \rightarrow ClO_2F + ClF \qquad (135)$$

9. *Miscellaneous*

Chlorine monoxide and sulfur trioxide have been found to form an addition compound which was first described as $Cl_2O \cdot 4SO_2$.[162] It was later discovered that ClO_2 gives the same compound, whose formula was now given[163] as $(ClO)(ClO_2)S_3O_{10}$.

Mixtures of chlorine monoxide and ammonia explode violently, possibly by the reactions[164] shown in eq 136 and 137.

$$3Cl_2O + 2NH_3 \rightarrow N_2 + 3H_2O + 3Cl_2 \qquad (136)$$

$$3Cl_2 + 8NH_3 \rightarrow 6NH_4Cl + N_2 \qquad (137)$$

Chlorine monoxide appears to play a role in some of the reactions of chlorine dioxide and catalyzes its hydrolytic decomposition.[165] The catalytic effectiveness of Cl_2O is characterized by a sharp maximum at 0.2×10^{-3} mol/l. of Cl_2O. It has also been found to catalyze the thermal decomposition of gaseous ClO_2 at 85 °C. Since the photolysis of ClO_2 follows the same kinetic law as the Cl_2O-catalyzed thermolysis, it has been suggested[166] that Cl_2O is an early product of the photolysis. This notion was later strengthened by the results of a study[167] of the stability of ClO_2 in CCl_4 solution. However, it was found that Cl_2O was slowly consumed, and the disappearance of ClO_2 follows the kinetics shown in eq 138.

$$-d[Cl_2O]/dt = k[ClO_2]^{4/3}[Cl_2O]^{1/3} \qquad (138)$$

Electrochemical reduction of Cl_2O can be achieved in 97 and 74% aqueous $HClO_4$, where it is not hydrolyzed and HOCl is dehydrated to Cl_2O.[168] The polarization curves for the Pt electrode, in these solutions, show an inflection at −1.70 V which is interpreted as resulting from the reduction of Cl_2O according to eq 139 and 140.

$$Cl_2O + 2H^+ + 2e^- \rightarrow Cl_2 + H_2O \qquad (139)$$

$$Cl_2O + 4H^+ + 4e^- \rightarrow 2HCl + H_2O \qquad (140)$$

When chlorine monoxide was first discovered, its reactivity toward various elements and compounds was tested.[169–171] Few details are available, but what little is known is summarized in Table XIX.

TABLE XIX. Miscellaneous Inorganic Reactions of Cl_2O

Reactant	Nature of reaction	Products	Ref
Se	Violent		1
P	Violent	P_2O_5, $POCl_3$	1
As	Violent	As_2O_5, $AsCl_3$	1
Br_2	Slow	ClBr, ClO_2, BrO_2	1, 169, 170
I_2	Slow	ClI, I_2O_5, $IOCl_3$	1, 169, 170
S	Violent	SO_2, S_2Cl_2	1
S (soln in S_2Cl_2)	Slow	$SOCl_2$	171
CS_2	Violent	$SOCl_2$, CO Cl, S_2Cl_2, SO_2	1
H_2S	Violent		1
C	Violent	O_2, Cl_2, CO_2	1
$(CN)_2$	Slow	CO_2, N_2, CNCl	1
PH_3	Violent		1
CO		$COCl_2$, CO_2	1
HCl		Cl_2, H_2O	1
Hg	Slow	$(HgO)_n$, $HgCl_2$	1
Ag	Slow	Ag_2O, Cl_2	1
S Ba			
S Sn	Violent	S_2Cl_2	1
S Hg			
$CaCl_2$ (moist)	Slow	$Ca(ClO)_2$, $Ca(ClO_3)_2$	1

D. Reactions with Organic Compounds

1. *Saturated Compounds*

The predominant reaction Cl_2O with organic compounds is chlorination, similar to that effected by chlorine, but differing significantly in that the by-product is not HCl, but water. Since the formation of a benign by-product may often be an advantage, it is surprising that the literature contains little evidence of efforts to develop chlorination by Cl_2O as an industrial process. In the USSR, the use of Cl_2O to produce chlorinated solvents, particularly carbon tetrachloride, has been found to give very good yields.[172,173] The procedure was conducted in two connected steps, of which the first was the preparation of Cl_2O by passing a mixture of chlorine and methane, at 20 °C, through a column containing HgO on pumice particles.[10] The emerging mixture, which contained methane (acting here as an inert diluting gas), Cl_2O, some unconverted Cl_2, and possibly some chlorinated methane, was then passed through a U-tube reactor, filled with an inert material and heated at high temperature. By this procedure, an initial mixture of 1 vol of CH_4 to 4 vol of Cl_2, reacting in the U-tube at 350 °C, gave quantitative conversion of the methane into CCl_4. At lower concentrations of chlorine, or lower temperatures, the chlorinated products were mixtures of CH_2Cl_2, $CHCl_3$, and CCl_4 in various proportions.

The gas-phase chlorination of propane by Cl_2O, at 100 °C, has been found to yield only 1- and 2-chloropropane (7:1 molar ratio) and hypochlorous acid.[174] Although the presence of oxygen, as a product of the straight pyrolysis of Cl_2O, might be predicted, none was detected. The mechanism proposed for the chlorination was a free-radical chain reaction, with ClO· as the main chain carrier, and the unimolecular decomposition of Cl_2O as the initiation step.

Later, however, the activation energy of the reaction was measured[175] as 11 kcal/mol, considerably lower than the 36 kcal/mol required for the homogeneous unimolecular decomposition of Cl_2O. Hence it was necessary to postulate another initiation step. The new proposal[175] was based on the presence of propene (≈0.1%) as an impurity in the propane used in these experiments. The propene would react as in eq 141 to initiate the formation of the chain-carrying (eq 142–145) ClO radicals. From this hypothesis, the overall rate of the reaction was calculated as $10^{-7.1}$ mol $l.^{-1}$ s^{-1} at 100°, in good agreement with the observed rate of $10^{-6.9}$.

$$C_3H_6 + Cl_2O \rightarrow C_3H_6Cl\cdot + ClO\cdot \qquad (141)$$

$$ClO\cdot + C_3H_8 \rightarrow CH_3\dot{C}HCH_3 + HOCl \qquad (142)$$

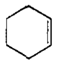
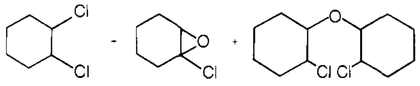
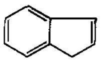
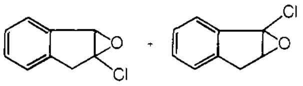
$$ClO\cdot + C_3H_8 \rightarrow CH_3CH_2\dot{C}H_2 + HOCl \qquad (143)$$

$$CH_3\dot{C}HCH_3 + Cl_2O \rightarrow CH_3CHClCH_3 + ClO\cdot \qquad (144)$$

$$CH_3CH_2\dot{C}H_2 + Cl_2O \rightarrow CH_3CH_2CH_2Cl + ClO\cdot \qquad (145)$$

The absence of the products of conceivable reactions constituting chain termination (eq 146–148) tends to confirm the

TABLE XX. Reactions of Unsaturated Compounds with Cl_2O

Reactant	Reagent	Products	Ref
$Cl_2C{=}CHCl$	Cl_2O (CCl_4)	$Cl_3CCHCl_2 + Cl_3CCHO + (Cl_3CCHCl)_2O$	177
$Cl_2C{=}CCl_2$	Cl_2O (CCl_4)	$Cl_3CCCl_3 + Cl_3CCHO$ (?)	177
	Cl_2O (CCl_4)		177
	Cl_2O (CCl_4)		177
$H(CF_2)_4CF{=}CF_2$	$Cl_2O + Cl_2$ (CCl_4)	$H(CF_2)_4CFClCOF + H(CF_2)_4CFClCF_2Cl$	178
$H(CF_2)_2CF{=}CF_2$	Cl_2O ($CCl_4 + H_2O$)	$H(CF_2)_2CFClCOOH$	178
$CFCl{=}CFCl$	Cl_2O (H_2O)	$(CFClH)_2 + CHF_2COOH$	178
$CF_2{=}CFCl$	$Cl_2O + Cl_2$ (CCl_4)	CF_3COF	178

large chain length ($\approx 10^4$) suggested by the kinetics of the gas-phase chlorination.

$$2C_3H_7\cdot \rightarrow C_6H_{14} \qquad (146)$$

$$C_3H_7\cdot + ClO\cdot \rightarrow C_3H_7OCl \qquad (147)$$

$$2ClO\cdot \rightarrow Cl_2 + O_2 \qquad (148)$$

Dissolved in CCl_4, each mole of Cl_2O will produce nearly 2 mol of chlorinated products and 1 mol of water (with a small amount of HCl accounting for the balance of the chlorine atoms) from various saturated compounds, such as 1-chlorobutane, 1-chloropropane, and *n*-butyronitrile.[23] When the reaction is conducted in the dark, there is a very long induction period. It is lengthened by the presence of oxygen or a decrease in temperature and shortened by exposure to light or addition of α,α'-azobisisobutyronitrile (AIBN). These observations suggest that the reaction in the dark is initiated by a slow thermal decomposition of Cl_2O (eq 149).

Another significant aspect of the liquid-phase chlorination is the selectivity exhibited by Cl_2O in abstracting hydrogen; the ratio is 1:11:24 for primary:secondary:tertiary. Thus, Cl_2O is more selective than Cl_2 (1:3.9:5.1), but less selective than *tert*-butyl hypochlorite (1:8:44). However, in various stages of the reaction of Cl_2O, changes occur in the product distribution and are such as to indicate an initial buildup of HOCl, with concomitant formation of products in a ratio indicative of the action of ClO radicals, followed by a decrease, accompanied by a less selective formation of chlorinated products, which indicates the action of Cl radicals. The mechanism proposed for chlorination in the liquid phase was accordingly proposed as a mixed radical chain (eq 149–155).

$$Cl_2O \rightarrow Cl\cdot + ClO\cdot \qquad (149)$$

$$ClO\cdot + RH \rightarrow HOCl + R\cdot \qquad (150)$$

$$R\cdot + Cl_2O \rightarrow RCl + ClO\cdot \qquad (151)$$

$$HOCl \rightarrow Cl\cdot + \cdot OH \qquad (152)$$

$$RH + Cl\cdot \rightarrow R\cdot + HCl \qquad (153)$$

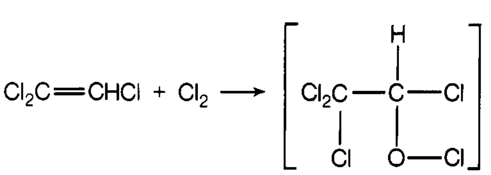
$$HCl + HOCl \rightarrow H_2O + Cl_2 \qquad (154)$$

$$R\cdot + Cl_2 \rightarrow RCl + Cl\cdot \qquad (155)$$

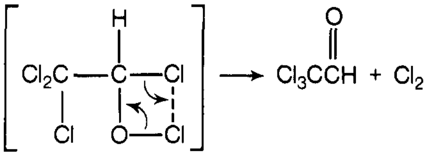
2. Unsaturated Compounds

Benzene was the first organic compound whose reaction with Cl_2O was investigated in any degree of detail.[176] It was reported to yield α- and β-benzene hexachlorides, and oxygen-containing compounds of the general formula $C_6H_6Cl_4O$; 2,4,6-trichlorophenol was identified as a minor product. Since 1900 there has been no published description of any attempt to repeat this reaction and confirm its results.

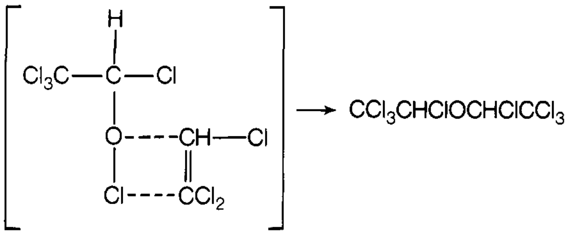
Research on the reactions of other unsaturated compounds has also been limited. The known results[177,178] are summarized in Table XX and accounted for by the speculative mechanism[177] (using trichloroethylene as an illustration) in which the chlorine monoxide first adds to the double bond (eq 156) and then either chlorine is split off leaving a carbonyl group (eq 157) or another molecule of olefin is added to yield an ether (eq 158).



(156)



(157)



(158)

It should be pointed out here that the rate of addition of HOCl to olefins has been found to be second order with respect to [HOCl].[179] Therefore it was suggested that the rate-determining step was the dehydration of HOCl (eq 159), and that Cl_2O is the active species in the chlorination.

$$2HOCl \rightleftarrows H_2O + Cl_2O \qquad (159)$$

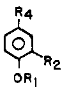
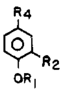
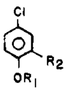
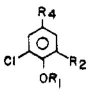
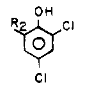
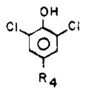
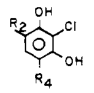
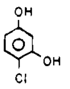
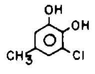
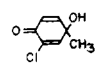
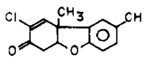
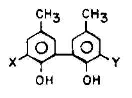
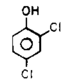
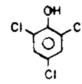
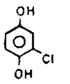
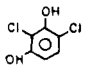
3. Phenols and Aryl Ethers

Table XXI shows the yields of products identified from the reaction of phenol, anisole, *o*- and *p*-cresol, respectively, with 0.5 mol of Cl_2O.[180] The reactions were conducted in CCl_4 solutions kept in the dark.

From the reaction of phenol, the ratio of *o*:*p*-chlorophenols produced, 2.9:1, is practically the same as that (2.8:1) obtained from the reaction with chlorine in carbon tetrachloride. This similarity was taken to indicate that chlorination with Cl_2O might follow a free-radical mechanism. The hypothesis was further reinforced by the isolation of *o*,*o'*-dicresol derivatives (I–III) and 2-chloro-4a,9b-dihydro-8,9b-dimethyl-3(4*H*)-dibenzofuranone (IV; a Pummerer's ketone) from the reaction with *p*-cresol, since these products are typical of those obtained from free-radical coupling reactions of phenols.[181]

When solutions (CCl_4) of *p*-cresol and Cl_2O were mixed, an

TABLE XXI. Reactions of Cl_2O with Phenols and Aromatic Ethers

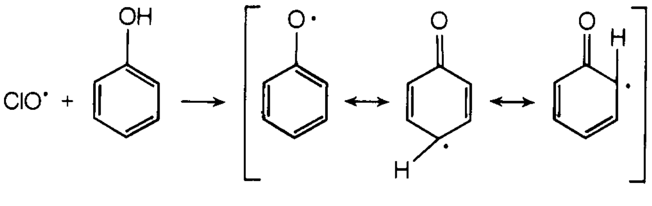
REACTANT	PRODUCTS							
	UNREACTED 							OTHER PRODUCTS
R_1 = H R_2 = H R_4 = H	0	21.9	64.5	4.7		0.05	0.2	————
R_1 = H R_2 = H R_4 = CH_3	20	—	46	—	TRACES	0.35	—	 1%  0.27%  IV : 1.5%  I : X=Y=H : 0.25% II : X=Y=Cl : 1.5% III : X=H, Y=Cl : 4%
R_1 = H R_2 = CH_3 R_4 = H	8.2	22	55	4	—	0.4	—	————
R_1 = CH_3 R_2 = H R_4 = H	24	41.2	20.1	TRACES	TRACES	0.05	0.1	 TRACES  0.2%  0.7%  0.5%

electron spin resonance signal was observed. Failure to detect free-radical signals from the reactions of phenol, *o*-cresol, and anisole was attributed to the short lifetime of the postulated free-radical intermediates.

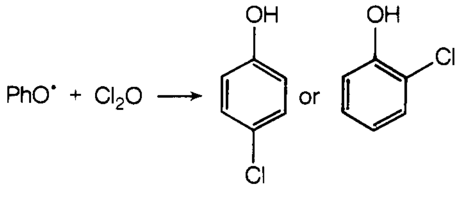
Color changes observed when diphenylpicrylhydrazyl (DPPH) was present in the reaction mixtures also suggested that free-radical intermediates played a role in the reaction.

Taken together, all this evidence suggested a free-radical mechanism (eq 160–163), akin to the one proposed for alkanes. The formation of hydroxylated products was accounted for by a reaction such as in eq 164.

$$Cl_2O \rightleftharpoons Cl^\bullet + ClO^\bullet \quad (160)$$

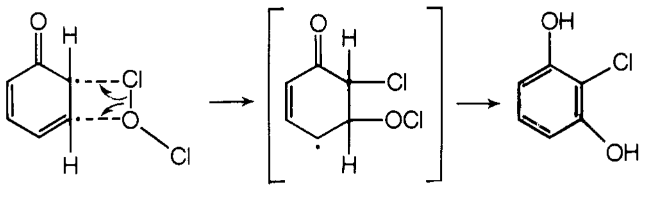


+ HOCl (161)



+ ClO˙ (162)

$$2HOCl \rightleftharpoons Cl_2O + H_2O \quad (163)$$



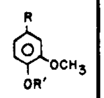
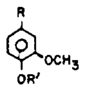
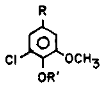
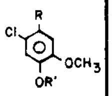
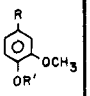
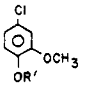
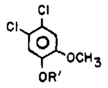
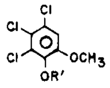
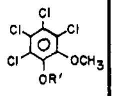
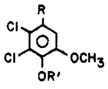
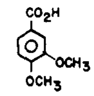
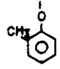
+ Cl˙ (164)

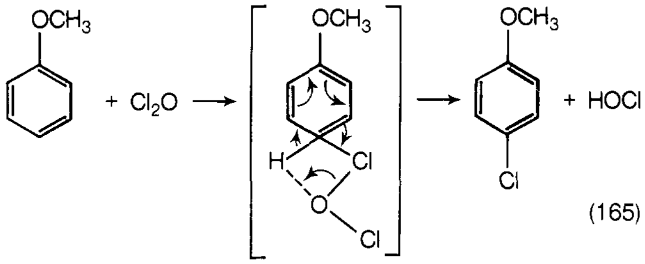
Later, the free-radical mechanism was seriously questioned.[182] Contrary evidence included the observation that Cl_2O reacts with DPPH, which is therefore not a good indicator of free radicals in the presence of this reagent. Moreover, the reaction of Cl_2O with chlorobenzene was not accelerated by the addition of a free-radical initiator (AIBN) or retarded by the presence of a free-radical scavenger (O_2). It was also observed that the rate of chlorination increased with the polarity of the solvent used and a large increase in the rate occurred when 5% trichloroacetic acid was added. Therefore, in place of the free-radical mechanism, an alternative was proposed, in which a polarized Cl_2O molecule attacked the aromatic ring. Equation 165 shows the mechanism as applied to anisole. Preponderance of the ortho chlorination of phenol by Cl_2O can be explained by the mechanism in eq 166.

As noted in section I, chlorine monoxide has recently been found to be an effective agent for the bleaching of wood pulps.[6,7] Accordingly, Table XXII presents the main results of reactions of Cl_2O with several compounds representing characteristic reactive units in the lignin macromolecule. As the table shows, a significant fraction of products come from displacement of the side chain, R, as might occur by the mechanism in eq 167.

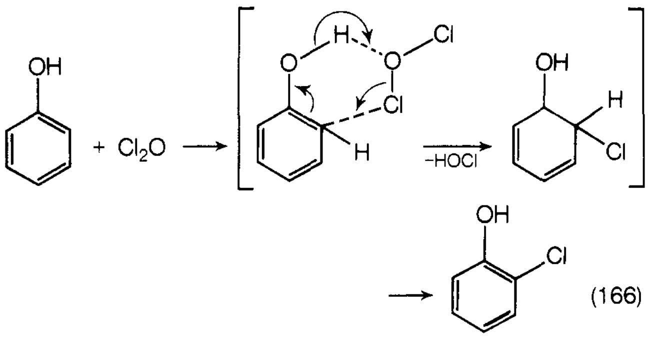
When insoluble lignin, isolated from wood by dissolution of the polysaccharides through periodate oxidation, was subjected

TABLE XXII. Reactions of Cl_2O with Lignin Model Compounds

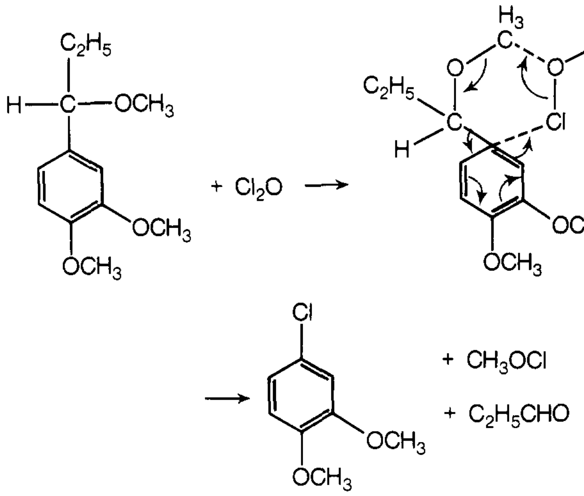
REACTANT	PRODUCTS									
	UNREACTED 									OTHER PRODUCTS
R = CHO R′ = H	—	80	—	—	—	—	—	—	—	—
R = CHO R′ = CH_3	48	3.0	6.8	3.3	—	1.2	—	—	—	37.7 % 
R = CHOH-C_2H_5 R′ = H	—	3	4	—	20	3	2	TRACES	0.7	—
R = $CH(OCH_3)$-C_2H_5 R′ = H	—	15-20	10	—	—	8-10	—	—	—	—
R = CHOH-C_2H_5 R′ = CH_3	—	—	20-30	—	—	8-10	TRACES	TRACES	—	—
R = $CH(OCH_3)$-C_2H_5 R′ = CH_3	—	—	11	—	TRACES	5	3.7	2.4	—	—
R = CHOH—CH—CH_2OH  R′ = CH_3	—	—	—	—	R′ = H TRACES	R′ = H: 10-15 R′ = CH_3 30-35	R′ = H 15-20	R′ = H 10	—	—



(165)



(166)



(167)

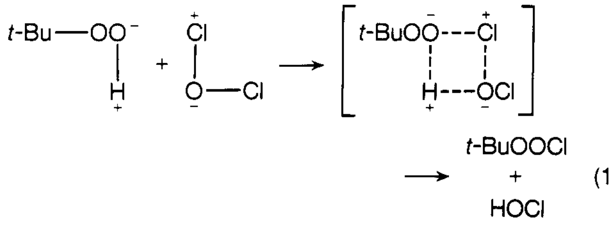
to the action of Cl_2O in CCl_4 solution, the presence of moisture (10% on lignin) was found essential for obtaining a solubilizing, degradative reaction, such as occurs in bleaching. At least 3 mol of Cl_2O was required per mole of lignin building block in order to ensure complete solubility of the treated lignin in dioxane. Gel permeation chromatography of the solubilized lignin showed two main fractions: one, at molecular weights narrowly distributed around 500, was interpreted as representing dimers and trimers of phenylpropane units; the other fraction was of a higher molecular weight, with its distribution centered around 5000. Elemental analysis of the products showed evidence of extensive chlorination as well as demethylation and oxidation. From these results, and those of the study of model compounds, a tentative mechanism was suggested[182] for the degradation of lignin by Cl_2O.

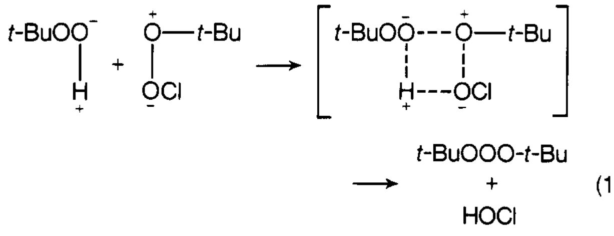
4. Miscellaneous

One other reaction of an aromatic compound, *N,N*-dimethylaniline, has been reported in the literature,[183] but few details were given. Products isolated included 50.5 mol % of unreacted starting material, 18.9 mol % of 2-chloro-*N,N*-dimethylaniline, 3.2 mol % of 4-chloro-*N,N*-dimethylaniline, and 1.2 mol % of 2,4-dichloro-*N,N*-dimethylaniline. This selectivity was comparable to that obtained by treating the same starting material with *tert*-butyl hypochlorite.

Other reactions of chlorine monoxide examined only superficially were those with acetone and ethyl acetoacetate, which yielded 1-chloro-2-propanone and α-chloroethyl acetoacetate, respectively.[177]

The reaction of Cl_2O with *tert*-butyl hydroperoxide, in CCl_3F solution at 0 °C, is characterized by an instantaneous liberation of oxygen.[184] At reaction temperatures below −30 °C, no oxygen is evolved at all. Since NMR spectroscopy at low temperature permitted the identification of *tert*-butylperoxy hypochlorite (*t*-BuOOCl) and di-*tert*-butyl trioxide (*t*-BuOOO*t*-Bu) as the main products, the reactions were formulated as in eq 168–170.


(168)


(169)

$$2HOCl \rightleftharpoons Cl_2O + H_2O \quad (170)$$

Initiation of the polymerization of methyl acrylate by the reaction mixture, as well as trapping experiments with an antioxidant, suggested that oxygen evolution proceeds via a peroxy radical whose formation is induced by di-*tert*-butyl trioxide.

VII. Addendum

Several pertinent articles and patents have appeared since this review was originally completed. One patent[185] deals with an improvement in the sodium carbonate method for generating Cl_2O gas. It claims that yields of over 90% were obtained by passing mixtures of chlorine and moist air, at room temperature and atmospheric pressure, over a highly porous form of Na_2CO_3 prepared by calcining pulverized $NaHCO_3$ at 150–400 °C.

It is encouraging to note that another patent,[186] as well as recent journal articles, describes reactions of Cl_2O with organic compounds, a subject largely neglected in the past. The patent describes a process for making 1,1,1-trichloroethane by means of the anhydrous reaction, in the liquid phase, in the dark, and at temperatures ranging from −20 to about 80 °C, of chloroethane, 1,1-dichloroethane, or a mixture of both with Cl_2O. Ethyl iodide, however, on treatment with Cl_2O, was found[187] to yield a complex mixture of ethyl chloride, diethyl ether, and ethyl acetate.

The reaction of Cl_2O with cyclohexene has been reinvestigated,[186] and, with the advantage of modern methods of analysis, nine products were detected, of which only two had been isolated in the previous investigation.[177] The main products have now been identified as 3-chlorocyclohexene (yield: 0.79 mol/mol of Cl_2O) and *trans*-2-chlorocyclohexanol (0.53 mol/mol of Cl_2O). Neither of these was reported as a product in the 1925 work, but the compound then assigned the postulated structure of chloroepoxycyclohexene may have been an artifact formed in the distillation of either the *trans*-2-chlorocyclohexanol or of the intermediate 2-chlorocyclohexyl hypochlorite. The mechanism proposed to account for the formation of nine products suggests that Cl_2O adds directly to the olefin to yield *trans*-2-chlorocyclohexyl hypochlorite, and simultaneously undergoes homolysis induced by the olefin, with which the free radicals then form addition and substitution products. Although the experimental evidence indicates that a free-radical mechanism predominates, ionic addition reactions cannot be ruled out for two of the products, the major product 3-chlorocyclohexene and the lesser product *trans*-1,2-dichlorocyclohexane (0.082 mol/mol of Cl_2O).

The potential of Cl_2O as a bleaching agent for wood pulp has recently been confirmed.[189]

VIII. References

(1) A. J. Balard, *Ann. Chim. Phys., Ser. 2,* **57,** 225 (1834).
(2) A. J. Balard, *Taylor's Sci. Mem.,* **1,** 269 (1837).
(3) J. L. Gay-Lussac, *C. R. Acad. Sci.,* **14,** 927 (1842).
(4) C. G. Swain and D. C. R. Crist, *J. Am. Chem. Soc.,* **94,** 3195 (1972).
(5) H. L. Robson in "Encyclopedia of Chemical Technology", Vol. 5, Wiley, New York, N.Y., 1964, pp 7–27.
(6) H. I. Bolker and N. Liebergott, *Pulp Pap. Mag. Can.,* **73,** T332 (1972).
(7) N. Liebergott and H. I. Bolker, U.S. Patent 3 619 349 (Nov 9, 1971).
(8) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. II, Longmans Green and Co., London, 1952, p 240.
(9) C. C. Addison, "Mellor's Treatise on Inorganic and Theoretical Chemistry", Vol. II, Suppl. 1, Wiley, New York, N.Y., 1956, p 514.
(10) V. M. Gallak, N. I. Belinskaya, and T. A. Pavlova, *Zh. Prikl. Khim. (Leningrad),* **38,** 1225 (1965); *J. Appl. Chem. USSR,* **38,** 1212 (1965).
(11) G. H. Cady, *Inorg. Synth.,* **5,** 156 (1957).
(12) M. Bodenstein and G. Kistiakowski, *Z. Phys. Chem.,* **116,** 371 (1925).
(13) C. F. Goodeve, *J. Chem. Soc.,* 2733 (1930).
(14) I. E. Muskat and G. H. Cady, U.S. Patent 2 155 281 (April 14, 1937).
(15) Y. Macheteau and J. Gillardeau, *Bull. Soc. Chim. Fr.,* 4075 (1967).
(16) C. J. Shack and C. B. Lindhal, *Inorg. Nucl. Chem. Lett.,* **3,** 387 (1967).
(17) R. L. Farrar, Jr., *U.S. A.E.C.,* **K-1416,** 1–33 (1960).
(18) V. Meyer, *Ber.,* **16,** 2998 (1883).
(19) J. D. Dunitz and K. Hedberg, *J. Am. Chem. Soc.,* **72,** 3108 (1950).
(20) G. Lunge and P. Naef, *Justus Liebigs Ann. Chem.,* **219,** 129 (1883).
(21) E. J. Bowen, *J. Chem. Soc.,* 1199 (1923).
(22) R. G. Dickinson and C. E. P. Jeffreys, *J. Am. Chem. Soc.,* **52,** 4288 (1930).
(23) D. D. Tanner and N. Nychka, *J. Am. Chem. Soc.,* **89,** 121 (1967).
(24) G. H. Cady, U.S. Patent 2 157 524 (May 9, 1939).
(25) G. H. Cady, U.S. Patent 2 157 525 (May 9, 1939).
(26) S. Goldschmidt, *Ber.,* **52B,** 753 (1919).
(27) W. A. Noyes and T. A. Wilson, *J. Am. Chem. Soc.,* **44,** 1630 (1922).
(28) W. A. Noyes and T. A. Wilson, *Recl. Trav. Chim. Pays-Bas,* **41,** 557 (1922).
(29) C. N. Hinshelwood, *Proc. R. Soc. London, Ser. A,* **131,** 177 (1931).
(30) J. W. T. Spinks, *J. Am. Chem. Soc.,* **53,** 3015 (1931).
(31) V. H. Dayan and B. C. Neale, *Adv. Chem. Ser.,* **No. 54,** 223 (1966).
(32) Z. Spurny, *Talanta,* **9,** 885 (1962).
(33) J. Pelouze, *Ann. Chim. Phys., Ser. 3,* **7,** 176 (1843).
(34) J. Pelouze, *C. R. Acad. Sci.,* **16,** 43 (1843).
(35) K. G. Thurnlackh and G. A. Schacherln, *Justus Liebigs Ann. Chem.,* **230,** 273 (1885).
(36) P. Harteck, *Z. Phys. Chem.,* **134,** 21 (1928).
(37) E. F. King and J. R. Partington, *J. Chem. Soc.,* 925 (1926).
(38) A. V. Pankratov, S. M. Rips, A. N. Zircheminov, and T. V. Kuznetsova, *Zh. Fiz. Khim.,* **42,** 380 (1968); *Russ. J. Phys. Chem.,* **2,** 198 (1968).
(39) S. M. Rips, A. N. Zercheminov, and A. V. Pankratov, *Zh. Fiz. Khim.,* **43,** 386 (1969); *Russ. J. Phys. Chem.,* **3,** 208 (1969).
(40) C. H. Secoy and G. H. Cady, *J. Am. Chem. Soc.,* **62,** 1036 (1940).
(41) W. Finkelnburg, H. J. Schumacher, and G. Stieger, *Z. Phys. Chem., Abt. B,* **15,** 127 (1931).
(42) "International Critical Tables", Vol. V, McGraw-Hill, New York, N.Y., 1928, p 176; J. Thomsen, *Thermo-chemische Untersuchungen, Leipzig,* **2,** 125 (1882).
(43) D. M. Yost and R. C. Felt, *J. Am. Chem. Soc.,* **56,** 68 (1934).
(44) W. H. Evans, T. R. Munson, and D. D. Wagman, *J. Res. Natl. Bur. Stand.,* **55,** Research Paper No. 2614.
(45) C. H. Secoy and G. H. Cady, *J. Am. Chem. Soc.,* **63,** 2504 (1941).
(46) W. A. Roth, *Z. Phys. Chem., Abt. A,* **145,** 289 (1929).
(47) J. I. Wallace and C. F. Goodeve, *Trans. Faraday Soc.,* **27,** 648 (1931).
(48) H. Mayer, Dissertation, Hannover, 1924; cited by C. H. Secoy and G. H. Cady, *J. Am. Chem. Soc.,* **63,** 2508 (1941).
(49) P. Gunther and K. Wekua, *Z. Phys. Chem., Abt. A,* **154,** 193 (1931).
(50) N. W. Luft, *J. Phys. Chem.,* **58,** 928 (1954).
(51) G. Nagarajan, *Bull. Soc. Chim. Belg.,* **72,** 16 (1963).
(52) K. Venkatesvarlu and R. Tahanalakshni, *Indian J. Pure Appl. Phys.,* **1,** 377 (1963).
(53) M. M. Rochkind and G. C. Pimentel, *J. Chem. Phys.,* **42,** 1361 (1965).
(54) D. S. Davis, *Ind. Eng. Chem.,* **34,** 624 (1942).
(55) B. Neumann and G. Muller, *Z. Anorg. Allg. Chem.,* **182,** 235 (1929).
(56) W. A. Roth, *Z. Phys. Chem., Abt. A,* **191,** 248 (1942).
(57) B. M. Israel, Doctoral Dissertation, University of Wisconsin, 1962; cited by ref 5.
(58) J. Ourisson and M. Kastner, *Bull. Soc. Chim. Fr.,* **6,** 1307 (1939).
(59) K. J. P. Orton and W. M. Gray, Report, 83rd Meeting of the British Association for the Advancement of Science, Birmingham, Sept 10–13, 1913, pp 136–141.
(60) F. G. Soper, *J. Chem. Soc.,* **125,** 2227 (1924).

(61) M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions", Pergamon Press, New York, N.Y., 1966, p 591.
(62) V. A. Kustodina, K. P. Mischenko, and I. E. Flis, *Zh. Prikl. Khim.*, **35,** 1374 (1962); *J. Appl. Chem. USSR*, **35,** 1319 (1962).
(63) I. E. Flis, K. P. Mischenko, and V. A. Kustodina, *Zh. Prikl. Khim.*, **34,** 306 (1961); *J. Appl. Chem. USSR*, **34,** 297 (1961).
(64) D. Sundhoff and H. J. Schumacher, *Z. Phys. Chem., Abt. B*, **28,** 17 (1935).
(65) I. P. Fisher, *Trans. Faraday Soc.*, **64,** 1852 (1968).
(66) I. P. Fisher, *J. Sci. Instr.*, **43,** 633 (1966).
(67) C. G. Freeman and L. F. Phillips, *J. Phys. Chem.*, **72,** 3025 (1968).
(68) H. F. Cordes and S. R. Smith, *J. Chem. Eng. Data*, **15,** 158 (1970).
(69) L. E. Sutton and L. O. Brockway, *J. Am. Chem. Soc.*, **57,** 473 (1935).
(70) L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **57,** 2684 (1935).
(71) L. Bru Villaseca, M. Perez-Rodriguez, and M. Cubero, *J. Chem. Phys.*, **20,** 1069 (1952).
(72) M. Perez-Rodrigues, R. Vega, and J. M. Garcia, *An. R. Soc. Esp. Fis Quim., Ser. A*, **49,** 5 (1953); *Chem. Abstr.*, **48,** 6254*h* (1954).
(73) B. Beagley, A. H. Clark, and T. G. Hewitt, *J. Chem. Soc. A*, 658 (1968).
(74) G. E. Herberich, R. H. Jackson, and D. J. Millen, *J. Chem. Soc. A*, 336 (1966).
(75) A. D. Baker, *Acc. Chem. Res.*, **3,** 17 (1970).
(76) A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *J. Chem. Phys.*, **55,** 2820 (1971).
(77) C. F. Goodeve and J. I. Wallace, *Trans. Faraday Soc.*, **26,** 254 (1930).
(78) G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions", New York, N.Y., 1939.
(79) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1105 (1954).
(80) A. E. Gilliam and R. A. Morton, *Proc. R. Soc. London, Ser. A*, **124,** 604 (1929).
(81) H. Martin and R. Gareis, *Z. Elektrochem.*, **60,** 959 (1956).
(82) C. R. Bailey and A. B. D. Cassie, *Nature (London)*, **129,** 652 (1932).
(83) C. R. Bailey and A. B. D. Cassie, *Proc. R. Soc. London, Ser. A*, **142,** 129 (1933).
(84) G. Hettner, R. Pohlman, and H. J. Schumacher, *Naturwissenschaften*, **23,** 114 (1935).
(85) W. G. Penny and G. B. B. M. Sutherland, *Proc. R. Soc. London, Ser. A*, **156,** 654 (1936).
(86) G. B. B. M. Sutherland and W. G. Penny, *Proc. R. Soc. London, Ser. A*, **156,** 678 (1936).
(87) K. Hedberg, *J. Chem. Phys.*, **19,** 509 (1951).
(88) L. Andrews and J. I. Raymond, *J. Chem. Phys.*, **55,** 3087 (1971).
(89) R. H. Jackson and D. J. Millen, *Proc. Chem. Soc., London*, 10 (1959).
(90) R. H. Jackson and d. J. Millen, *Adv. Spectrosc.*, **3,** 1157 (1962).
(91) D. J. Gardiner, *J. Mol. Spectrosc.*, **38,** 476 (1971).
(92) B. Beagley, A. H. Clark, and D. W. J. Cruickshank, *Chem. Commun.*, 458 (1966).
(93) E. A. Robinson, *Can. J. Chem.*, **41,** 3021 (1963).
(94) S. Smith and J. W. Linnett, *Trans. Faraday Soc.*, **52,** 891 (1956).
(95) K. Venkateswarlu and R. Thanalakshui, *J. Annamalai Univ., Part B*, **24,** 13 (1962); *Chem. Abstr.*, **59,** 10773*h* (1963).
(96) K. Venkateswarlu and P. Thirugnanasambandam, *Z. Phys. Chem. (Leipzig)*, **212,** 138 (1959).
(97) T. Oka and Y. Morita, *J. Mol. Spectrosc.*, **8,** 9 (1962).
(98) S. N. Thakur and S. N. Rai, *J. Mol. Struct.*, **5,** 320 (1970).
(99) A. Natarajan and R. Ramasamy, *Indian J. Pure Appl. Phys.*, **10,** 12 (1972).
(100) M. Mohan and A. Mueller, *Chem. Phys. Lett.*, **14,** 205 (1972).
(101) R. Srinivasamoorthy, S. Jeyapandian, and G. A. Savari Raj, *Chem. Phys. Lett.*, **14,** 493 (1972).
(102) F. K. Chi and L. Andrews, *J. Phys. Chem.*, **77,** 3062 (1973).
(103) V. I. Durakov and S. S. Batsanov, *Zh. Strukt. Khim.*, **2,** 456 (1961); *Chem. Abstr.*, **57,** 4051*i* (1962).
(104) E. L. Wagner, *J. Chem. Phys.*, **37,** 751 (1962).
(105) F. S. Mortimer, *Adv. Chem. Ser.*, **No. 54,** 39 (1966).
(106) T. Iredale and T. G. Edwards, *J. Am. Chem. Soc.*, **59,** 761 (1937).
(107) E. J. Bowen, *J. Chem. Soc.*, **123,** 2380 (1923).
(108) H. J. Schumacher and R. V. Townend, *Z. Phys. Chem., Abt. B*, **20,** 375 (1933).
(109) H. J. Schumacher and C. Wagner, *Z. Phys. Chem., Abt. B*, **5,** 199 (1929).
(110) A. G. Brown and J. W. T. Spinks, *Can. J. Res., Sect. B*, **15,** 113 (1937).
(111) J. W. T. Spinks and J. M. Porter, *J. Am. Chem. Soc.*, **56,** 343 (1934).
(112) J. Franck and A. Euckey, *Z. Phys. Chem., Abt. B*, **20,** 460 (1933).
(113) F. H. C. Edgecombe, R. G. W. Norrish, and B. A. Thrush, *Proc. R. Soc. London, Ser. A*, **243,** 24 (1957).
(114) N. Basco and S. K. Dogra, *Proc. R. Soc. London, Ser. A*, **323,** 401 (1971).
(115) M. M. Rochkind and G. C. Pimentel, *J. Chem. Phys.*, **46,** 4481 (1967).
(116) W. G. Alcock and G. C. Pimentel, *J. Chem. Phys.*, **48,** 2373 (1968).
(117) C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **123,** 2730 (1923).
(118) J. J. Beaver and G. Stieger, *Z. Phys. Chem., Abt. B*, **12,** 93 (1931).
(119) M. Bodenstein and Z. Szabo, *Math. Naturw. Anz. Ungar. Akad. Wiss.*, **57,** 613 (1938); *Chem. Abstr.*, **33,** 2022 (1939).
(120) M. Bodenstein and Z. Szabo, *Z. Phys. Chem., Abt. B*, **39, 44** (1938).
(121) Z. O. Szabo, *Magy. Kem. Foly.*, **56,** 109 (1950); *Chem. Abstr.*, **45,** 862*d* (1951).
(122) E. A. Moelwyn-Hughes and C. N. Hinshelwood, *Proc. R. Soc. London*, **131,** 177 (1931).
(123) C. N. Hinshelwood and J. Hughes, *J. Chem. Soc.*, **125,** 1841 (1924).
(124) C. N. Hinshelwood and C. W. Thornton, *Philos. Mag.*, **50,** 1135 (1925).
(125) H. Eyring, *Z. Phys. Chem., Abt. B*, **7,** 244 (1930).
(126) H. Damianovitch, *Gazz. Chim. Ital.*, **59,** 568 (1929).
(127) P. Huhn, *Magy. Kem. Foly.*, **58,** 380 (1952); *Chem. Abstr.*, **47,** 5225*g* (1953).
(128) H. Guenebaut and C. Couet, *C. R. Acad. Sci.*, **256,** 2613 (1963).
(129) N. N. Semenov, *Phys. Z. Sowjetunion*, **1,** 561 (1932); *Chem. Abstr.*, **26,** 5482 (1932).
(130) J. Zawidski, *Rocz. Chem.*, **5,** 504 (1925); *Chem. Abstr.*, **21,** 11 (1927).
(131) D. Pilipovitch, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, *Inorg. Chem.*, **11,** 2189 (1972).
(132) G. H. Cady and R. E. Brown, *J. Am. Chem. Soc.*, **67,** 1614 (1945).
(133) G. Pannetier and M. Ben Caid, *Bull. Soc. Chim. Fr.*, 1628 (1961).
(134) A. B. Sagulin, *Z. Phys. Chem., Abt. B*, **1,** 275 (1928).
(135) C. G. Freeman and L. F. Phillips, *J. Phys. Chem.*, **72,** 3031 (1968).
(136) M. J. Perona, D. W. Setser, and R. J. Johnson, *J. Phys. Chem.*, **73,** 2091 (1969).
(137) M. J. Perona, D. W. Setser, and R. J. Johnson, *J. Chem. Phys.*, **52,** 6384 (1970).
(138) M. C. Lin, *Chem. Phys. Lett.*, **7,** 209 (1970).
(139) G. G. Freeman and L. F. Phillips, *J. Phys. Chem.*, **72,** 3028 (1968).
(140) P. Pierron, *Bull. Soc. Chim. Fr.*, **8,** 660 (1941).
(141) P. Pierron, *Bull. Soc. Chim. Fr.*, **8,** 664 (1941).
(142) V. A. Kustodina, K. P. Mishchenko, and I. E. Flis, *Zh. Prikl. Khim.*, **34,** 125 (1961); *J. Appl. Chem. USSR*, **34,** 117 (1961).
(143) K. P. Mishchenko, I. E. Flis, K. Yu. Salnis, V. A. Kustodina, and N. V. Pakhomova, *Khim. Perekisnykh. Soedin. Akad. Nauk SSR, Inst. Obshch. i Neorg. Khim.*, 53 (1963); *Chem. Abstr.*, **61,** 5017g (1964).
(144) H. Martin, *Angew. Chem.*, **70,** 97 (1958).
(145) H. Martin and W. Meise, *Z. Elektrochem.*, **63,** 162 (1959).
(146) H. Martin, W. Meise, and E. Engelmann, *Z. Phys. Chem. (Frankfurt am Main)*, **24,** 285 (1960).
(147) H. Martin, *Angew. Chem., Int. Ed. Engl.*, **5,** 78 (1966).
(148) H. Martin, J. Robisch, J. Knauth, and K. G. Prusseit, *Z. Phys. Chem. (Frankfurt am Main)*, **77,** 227 (1972).
(149) M. Schmeisser, W. Fink, and K. Brandle, *Angew. Chem.*, **69,** 780 (1957).
(150) H. Barbes and P. Vast, *Rev. Chim. Miner.*, **8,** 851 (1971).
(151) C. J. Shack and D. Pilipovitch, *Inorg. Chem.*, **9,** 387 (1970).
(152) C. J. Shack and D. Pilipovitch, *Am. Chem. Soc., Div. Fuel Chem., Prepr.*, **12,** 85 (1968).
(153) Z. K. Nikitina, V. Ya. Rosolovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 273 (1973); *Chem. Abstr.*, **79,** 143 328*j* (1973).
(154) K. Dehnicke, *Chem. Ber.*, **97,** 3354 (1964).
(155) K. Dehnicke, *Chem. Ber.*, **97,** 3358 (1964).
(156) K. Dehnicke, *Z. Anorg. Allg. Chem.*, **308,** 72 (1961).
(157) K. Dehnicke, *Z. Anorg. Allg. Chem.*, **309,** 266 (1961).
(158) K. Dehnicke, *Z. Anorg. Allg. Chem.*, **312,** 237 (1961).
(159) K. Dehnicke, A. F. Shihada, *Z. Naturforsch. B*, **28,** 148 (1973).
(160) P. P. Kornuta and V. I. Shevchenko, *Zh. Obshch. Khim.*, **40,** 551 (1970); *J. Chem. USSR*, **40,** 517 (1970).
(161) C. J. Shack, C. B. Lindahl, D. Pilipovitch, and K. O. Christe, *Inorg. Chem.*, **11,** 2201 (1972).
(162) A. A. Woolf, *Chem. Ind. (London)*, 1320 (1954).
(163) H. A. Lehmann and G. Kruger, *Z. Anorg. Allg. Chem.*, **274,** 141 (1953).
(164) R. Schwarz and H. Striebich, *Z. Anorg. Allg. Chem.*, **224,** 29 (1935).
(165) R. W. Brown, *Tappi*, **35,** 75 (1952).
(166) H. Booth and E. J. Bowen, *J. Chem. Soc.*, **127,** 510 (1925).
(167) R. Luther and R. Hoffmann, *Z. Phys. Chem., Abt. A*, **177,** 17 (1936).
(168) A. E. Missan and A. M. Sukhotin, *Zh. Neorg. Khim.*, **4,** 606 (1959); *Russ. J. Inorg. Chem. (Engl. Transl.)*, **4,** 276 (1959).
(169) P. Schutzenberger, *C. R. Acad. Sci.*, **53,** 538 (1861).
(170) P. Schutzenberger, *Ber.*, **2,** 218 (1869).
(171) A. Wurtz, *C. R. Acad. Sci.*, **62,** 460 (1866).
(172) V. M. Gallak, N. I. Belinskaya, and T. A. Pavlova, *Zh. Prikl. Khim.*, **38,** 2599 (1965); *J. Appl. Chem. USSR*, **38,** 2537 (1965).
(173) V. M. Gallak and N. I. Belinskaya, USSR Patent 181 068 April 15, (1966); Appl. Dec 18, 1962; *Chem. Abstr.*, **65,** 8759*c* (1966).
(174) L. Phillips and R. Shaw, *Proc. Chem. Soc. (London)*, 294 (1962).
(175) R. Shaw, *J. Chem. Soc. B*, 513 (1968).
(176) R. Scholl and W. Norr, *Ber.* **33,** 723 (1900).
(177) S. Goldschmidt and H. Schussler, *Ber.*, **58B,** 566 (1925).
(178) S. V. Sokolov, V. S. Yuminov, and L. N. Pushkina, *Zh. Obshch. Khim.*, **35,** 2150 (1965); *Chem. Abstr.*, **64,** 11074*c* (1966).
(179) E. A. Shilov, G. V. Kupinskaya, and A. A. Yasnikov, *Dokl. Akad. Nauk SSSR*, **81,** 435 (1951); *Chem. Abstr.*, **46,** 3376*d* (1952).
(180) M. Fujii, Ph.D. Thesis, McGill University, Montreal, 1969.
(181) H. Musso in "Oxidative Coupling of Phenols", W. L. Taylor and A. R. Battersby, Ed., Marcel Dekker, New York, N.Y., 1967.
(182) K. S. Lee, M.S. Thesis, McGill University, Montreal, 1973.
(183) T. H. Chao and L. P. Cipriani, *J. Org. Chem.*, **26,** 1079 (1961).
(184) J. Van Ham, A. Schors, and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **92,** 393 (1973).
(185) W. A. Mueller, German Offen. 2 326 601 (Dec 12, 1974); British Patent 1 358 839 (July 3, 1974); Canadian Patent 952 285 (Aug 6, 1975).
(186) G. L. Kochanny, Jr., and T. A. Chamberlin, U. S. Patent 3 872 176 (March 18, 1975).
(187) K. Baum and C. D. Beard, *J. Org. Chem.*, **40,** 2536 (1975).
(188) D. D. Tanner, N. Nychka, and T. Ochiai, *Can. J. Chem.*, **52,** 2573 (1974).
(189) C. Christiansen and R. D. Friedt, *Paper Trade J.*, **159** (23), 44 (1975).