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INORGANIC SULFUR REAGENTS. I: THE THIONYL HALIDES*

By

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Introduction

Our studies of organic sulfur compounds have made us increasingly aware of the inorganic sulfur reagents. While it is clear that many compounds of this group have now become of greatest theoretical and practical interest, yet there has been a lack of correlative and review papers which would serve to focus attention on them. Since we had much of the required literature at hand, it seemed desirable to prepare a series of brief articles, each of which would give a thorough entry to the literature on a selected group of these substances.

The present paper concerns the thionyl halides, SOX_2. The known examples of this group of compounds are shown in Table I, together with the other known compounds of sulfur and halogen, and of sulfur, oxygen and halogen. Part II of this series will present the sulfuryl halides, SO_2X_2.

THIONYL CHLORIDE

Physical Properties

Thionyl chloride, $SOCl_2$, melts at -104.5°, boils at 78.8°, has a density (at 14.5°) of 1.656 g./ml. and a refractive index, n_D^{10}, of 1.517.[1]

Pure thionyl chloride is a colorless, fuming, toxic, irritating liquid which is miscible with benzene, carbon tetrachloride, chloroform and most inert organic solvents. Studies involving force constants,[2,3] infrared,[4,5,6] Raman,[7-10] and ultraviolet[11] spectra, magnetic rotatory power,[12] magnetic susceptibility[13], and dielectric constants and dipole moments[14,15] have been carried out. Its physical properties have suggested its frequent use as an ionizing solvent.[16-20] The heat of formation of thionyl chloride is -58.5 Kcal./mole.[21]

Preparation

The first preparations of thionyl chloride employed the reactions of sodium sulfite with phosphorus pentachloride[22] and of calcium sulfite with phosphorus oxychloride.[23] Industrial methods, described in the patent literature,[25-31] have sought less expensive syntheses, examples of which are shown in the following equations:

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(1)[24, 31] $SCl_2 + SO_3 \xrightarrow{SbCl_3} SO_2 + SOCl_2$

(2)[25] $S_2Cl_2 + 2\,SO_2 + 3\,Cl_2 \xrightarrow{C} 4\,SOCl_2$

(3)[26] $CO + Cl_2 + SO_2 \xrightarrow{C} SOCl_2 + CO_2$

(4)[27] $2\,S + O_2 + 2\,Cl_2 \xrightarrow{\text{catalyst}} 2\,SOCl_2$

(5)[28, 29] $SO_2 + CCl_4 \xrightarrow{AlCl_3} SOCl_2 + COCl_2$

In the process of equation 1, sulfur dichloride may be prepared <u>in situ</u> from sulfur monochloride and chlorine ($ClSSCl + Cl_2 \longrightarrow 2\,ClSCl$).[a]

The sulfur trioxide is usually introduced by using fuming sulfuric acid. Excess sulfur trioxide must be avoided because of the easy formation of the so-called "pyrosulfuryl chloride" (equation 6). If radioactive SCl_2 is used

(6) $SOCl_2 + 2\,SO_3 \longrightarrow S_2O_5Cl_2 + SO_2$

in the method of equation 1, the tagged sulfur is found mainly in the thionyl chloride.[32]

Considering the reaction of equation 2: sulfur dichloride may be substituted for sulfur monochloride and part of the chlorine, and sulfuryl chloride may be used as a source of SO_2 and Cl_2. The reaction is best carried out at 150-200°. With recycling of the sulfur chlorides, SO_2 and SO_2Cl_2 which are formed, nearly 100% conversion is reported. At high temperatures (500°), the decomposition of thionyl chloride is nearly complete. At intermediate temperatures (198° and 238°), the system, $SO_2Cl_2 + SCl_2 \rightleftharpoons 2\,SOCl_2$, represents a reversible reaction.[30] The oxidation of SCl_2 with oxygen, to give sulfuryl chloride is irreversible under these conditions. Equation 7 represents an overall procedure which has been used to prepare thionyl chloride.[30]

(7) $2\,SCl_2 + O_2 \xrightarrow{C(\text{activated})} 2\,SOCl_2$

Phosgene may also be employed in reaction 3.

In reaction 5, the yield of thionyl chloride is 72%. Substitution of chloroform or pentachloroethane for carbon tetrachloride lowers the yield to 40% and 6%, respectively.

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[a] This chlorinolysis of the sulfur-sulfur bond is a very general reaction, and has found many applications in organic chemistry. The products obtained are sulfenyl chlorides: $2\,RSSR + Cl_2 \longrightarrow 2\,RSCl$. Cf. e.g., Organic Sulfur Compounds, Vol. 1, edited by N. Kharasch, Pergamon Press (1960): Chs. 31 and 32.

The reaction of boron trichloride with the sulfur dioxide, in which the latter acts as solvent, is extremely slow unless chloride ion is present.[33] It has been suggested that the catalytic effect of chloride ion may involve the ion, SO_2Cl^-.

(8) $$2\ BCl_3 + 3\ SO_2 \xrightarrow{Cl^-} 3\ SOCl_2 + B_2O_3$$

Technical grade thionyl chloride contains about 7% impurities, mainly sulfur monochloride, sulfuryl chloride and sulfur dioxide.[34] Sulfur monochloride may be removed after reaction with sulfur, and the sulfuryl chloride may be taken out by means of its selective reaction with other substances.[34] Reagent grade thionyl chloride is also available.

Chemical Properties

Above its boiling point, thionyl chloride decomposes to sulfur chloride, sulfuryl chloride, sulfur dioxide, and chlorine. The photochemistry of thionyl chloride does not seem to have been investigated in detail, but seems worthy of study, especially in comparison with sulfuryl chloride.

Rapid sulfur exchange between S^*OCl_2-$SOBr_2$ and $SOCl_2$-S^*OBr_2 in SO_2 solution at -50° or in mixtures of pure compounds at -20° has been observed.[35] Similarly, chlorine exchanges rapidly between Cl^*-labelled pyridinium chloride and $SOCl_2$ in chloroform at 20°.[36] These results may be accounted for by the ionization of the thionyl halides or the formation of addition complexes and are in marked contrast to results wherein the lack of exchange between S^*OCl_2 and SO_2Cl_2 has been noted.[35]

Thionyl chloride reacts with metals, such as antimony, sodium, aluminium, magnesium, and iron. The reactions are generally slow in the absence of acids[37] (except in the case of antimony) and this explains the use of iron containers for storage of the thionyl chloride. Glass, lead, and nickel containers are also used for storage.

With phosphorus, selenium and tellurium, reaction with thionyl chloride yields the respective chlorides.

Hydrated chlorides, such as $MgCl_2 . 6\ H_2O$, are conveniently dehydrated with $SOCl_2$, since the products, HCl and SO_2, are gases.[39] Mustard gas may also be dried in this way.[40]

In some of its inorganic reactions, thionyl chloride acts as an oxidising agent, e.g.:

(9) $$4\ HI + 2\ SOCl_2 \longrightarrow 2\ I_2 + 4\ HCl + SO_2 + S$$

(10) $$2\ H_2S + 2\ SOCl_2 \xrightarrow{AlCl_3} 4\ HCl + SO_2 + 3\ S$$

In other reactions, however, it functions as the reducing agent:

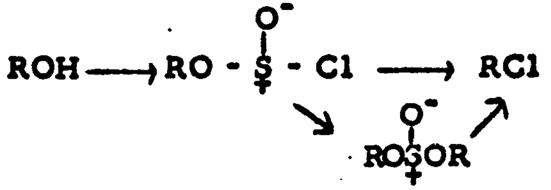
(11) $$2\ HNO_3 + SOCl_2 \longrightarrow H_2SO_4 + NO_2Cl + NOCl$$

(12) $$N_2O_4 + SOCl_2 \longrightarrow 2\ NOCl + SO_3$$

The reaction with silver nitrate yields silver chloride and $Cl\overset{O}{\overset{\|}{S}}ONO_2$, while with ammonia, polymeric thionylimine, $(HNSO)_x$, is reported as the product.[41] The preparation of chromyl chloride using CrO_3 or $K_2Cr_2O_7$ has been mentioned.[42]

The best known reactions of thionyl chloride in organic chemistry involve the replacement of hydroxyl groups, in alcohols and carboxylic acids, by chlorine. The conversion of alcohols to alkyl halides often occurs with retention of configuration. This is not, however, always the case. The steps involved in the reaction converts the alcohol to chlorosulfinates and, in some instances, to sulfites. Under certain conditions these intermediates can be isolated.

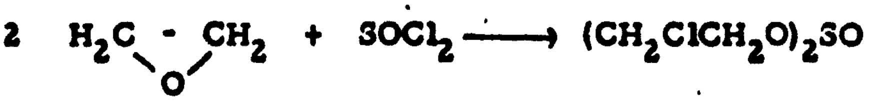
(13)



The elimination of sulfur dioxide from the chlorosulfinates may occur through different transition states.

The detailed mechanism and stereochemistry has been studied in a number of investigations with alcohols,[32, 46, 47, 48] with small ring alcohols,[49] with chlorocyclohexanols,[50] with allylic alcohols,[51] with acylamino alcohols,[52] and with sterols.[53, 54] The widely used reaction for conversion of acids to acid chlorides has been shown to occur through the carboxylic anhydride when pyridine is employed.[55] Sulfonic acids and carboxylic acids, which do not normally react with thionyl chloride, do so in the presence of dimethylformamide.[56] The ionized salt $(CH_3)_2NCHCl^+Cl^-$, is formed. Another interesting application involves the estimation of the number of carboxyl groups in gelatin with $SOCl_2$ and CH_3OH.[57] 2-Naphthoic acid, heated with thionyl chloride at 180-200°, yields 1, 6-dichloronaphthalene. Mercapto groups are replaced by chlorine and some ketones are converted to vinyl chlorides by $SOCl_2$.[59] Ethylene oxides yield 2-chloro sulfites[60] while aliphatic β-lactones give 3-chloroalkanoyl chlorides.[61]

(12)



$$2\ H_2C - CH_2\ (O) + SOCl_2 \longrightarrow (CH_2ClCH_2O)_2SO$$

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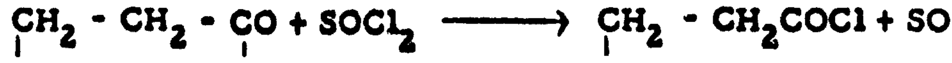

$$CH_2 - CH_2 - CO + SOCl_2 \longrightarrow CH_2 - CH_2COCl + SO_2$$

Thionyl chloride cleaves cyclic ethers and related compounds to afford dichloro derivatives. Examples are the reaction with tetrahydrofuran[62] and 4-phenyl-1,3-dioxane.[63] Another interesting ether cleavage involves the

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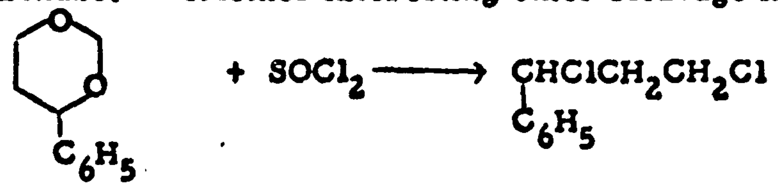
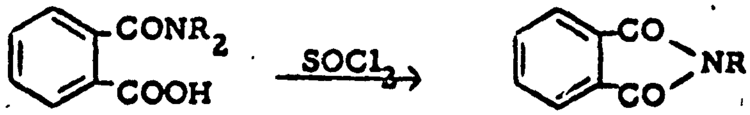


conversion of γ-methoxyvaleric acid to methyl γ-chlorovalerate with inversion at the γ-carbon atom.[64]

The products of the reaction of $SOCl_2$ with phenols are dependent on the conditions. In some instances sulfites can be obtained and under other conditions ring substitution occurs. The reactions of this type have been reviewed.[65] In general, the Friedel-Crafts reaction with $SOCl_2$ is not very successful, but 9-fluorenyl[66] and *p*-acetamidophenyl[67] sulfoxide may be prepared in this way. In the presence of copper, $SOCl_2$ and substituted phenols (4-hydroxycoumarin,[68] 4-propionylresorcinol,[69] 2-hydroxy-5-methylacetophenone,[70] and the naphthols[71]) yield symmetrical sulfides by ring substitution and attendant reduction.

Thionyl chloride is an effective agent for intramolecular removal of the elements of water. Examples are the dehydration of 1,1,1-trichloro-2-methyl-2-propanol, which occurs *via* the chlorosulfinate and which is catalyzed by amines,[72] and ethyl 2-carbomethoxy-1-hydroxy-2-methyl cyclohexylacetate.[73] The units of alcohol are similarly removed from a substituted phthalamic acid[74] and water is removed intermolecularly from oxanilic acid.[75] Urea is converted to cyanuric acid and other products.[76, 77]

(15)



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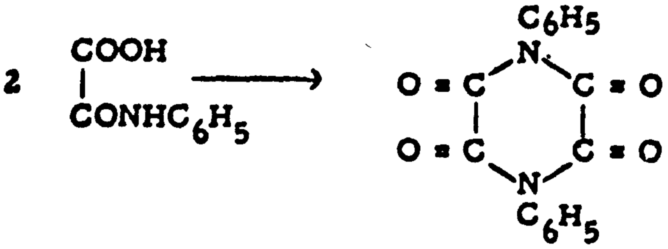


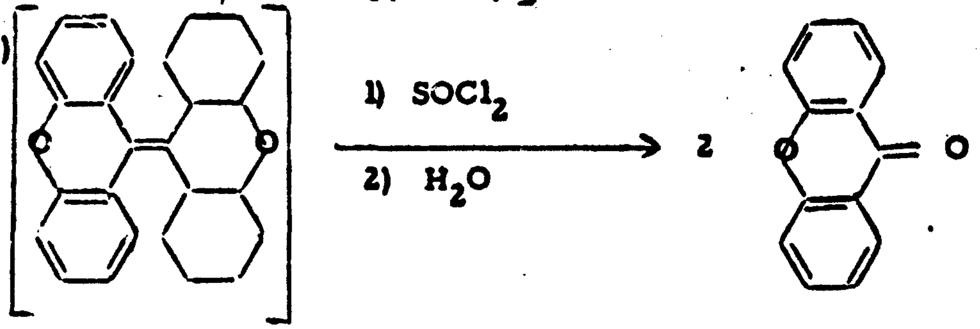
The intermolecular condensation of glucose is also effected through the use of thionyl chloride.[78]

Chlorination of compounds with thionyl chloride is illustrated by the reaction with dimethyl sulfide.[79] For these purposes, thionyl chloride is a less vigorous agent than sulfuryl chloride and promotes formation of mono and dichloro derivatives, rather than higher chlorinated products. The addition of chlorine to benzene is activated by the presence of thionyl chloride and the amount of the gamma isomer of hexachlorocyclohexane may be affected by its presence [80, 81] In the special case of 1, 1-diarylethylenes, sulfinic acid is obtained[82] after hydrolysis of the product. Chlorophenothiazines are chlorinated by thionyl chloride.[83] Alternatively, the phenothiazine ring may be closed with the chlorination by the action of thionyl chloride on diphenylamine.

$$Ar_2C = CH_2 + SOCl_2 \longrightarrow Ar_2C = CHSO_2H \qquad (17)$$

The oxidative character of thionyl chloride is sometimes exhibited in organic reactions. The cleavage of substituted $\Delta^{9,9'}$-bixanthenes to xanthones[84, 85, 86] and the dehydrogenation of a highly hindered acrylic acid, cis-o- [4, 5-(1', 2'-naphtho)-3-pyrazolyl] cinnamic acid, to the corresponding propiolic acid[87] are examples.

(18)



Thionyl chloride is not usually the best reagent for effecting the Beckmann rearrangement because it initiates cleavage reactions.[88] The conversion of cyclohexanone oxime to epsilon-caprolactam with thionyl chloride occurs with fair results, however.[89]

Primary aromatic amines are converted to thionylimines, $ArN = SO$, with $SOCl_2$.[90] 8-Thiapurines are obtained by the reaction of thionyl chloride with 5, 6-diaminouracils.[91] Other thiadiazoles are obtained through the use of orthodiamines.[92] The cleavage of sulfinyl esters by $SOCl_2$[93] and its addition to ketene to give after methanolysis $(MeOOCCH_2)_2SO$ [94] are further interesting applications. Its reaction with phenylarsine to give C_6H_5AsS[95] contrasts with the reaction of phenylphosphine with $SOCl_2$, which yields $(C_6H_5PSO)_3$.[96] $C_6H_5As(MgBr)_2$ and $SOCl_2$ gives C_6H_5AsSO.

A possible application of thionyl chloride, which has not been exploited fully as yet, is its chain terminating properties. It has been shown that $SOCl_2$ acts in this way in the sulfoxidation of cyclohexane (reaction with SO_2 and O_2, under irradiation).[97]

Reviews on the early chemistry of $SOCl_2$,[23] the reaction with phenol,[65] with *p*-aminobenzoic acid,[98] synthetic applications,[99] and technology[100] have appeared.

THIONYL FLUORIDE

Thionyl fluoride, SOF_2, melts at -129.5° and boils at -43.8°[101]. Raman,[102, 103] infrared,[104] and microwave[105] spectra, dipole moment[105] and force constant studies have been carried out. Thionyl fluoride is obtained by the reaction of thionyl chloride with AsF_3, SbF_3,[106, 107] HF,[108] or KSO_2F,[109, 110] by reaction of S_4N_4 with aqueous HF and CuO,[111] and by reaction of SO_2 with VF_5.[112] A 77% yield was obtained recently by reaction of sodium fluoride with thionyl chloride in acetonitrile.[113]

Thionyl fluoride hydrolyzes slowly, but completely at room temperature, forming sulfurous and hydrofluoric acid. Thermally, however, it is quite stable.[106] With SiO_2 at 400°, thionyl fluoride gives SiF_4 and SO_2. Mixtures of SOF_2 and O_2, submitted to an electric discharge, give peroxy compounds.[114]

THIONYL CHLOROFLUORIDE

Thionyl chlorofluoride, SOClF, boils at 12.2°, melts at -139.5°, and has a liquid density of 1.580 g./ml.[101] It is prepared by the action of SbF_3 and $SbCl_5$[101] or IF_5.[115] on $SOCl_2$. The chlorofluoride reacts with mercury and copper, at room temperature, and with iron at 70°. The overall reaction is represented by equation 19. (M = metal).

$$(19) \qquad 4\,SOClF + 3\,M \longrightarrow 2\,SOF_2 + SO_2 + MCl_2 + 2\,MS$$

Disproportionation may occur first; if so, the products are those of the reaction of $SOCl_2$ with the metal.[101]

THIONYL BROMIDE

Thionyl bromide, $SOBr_2$, melts at -52°, boils at 138° (decompn.), at atmospheric pressure or at 42.5° at 16 mm. pressure, has a density at 15° of 2.698 and is an orange-yellow liquid.[116] Raman spectrum.[117] Thionyl bromide is prepared by the reaction of HBr or KBr with $SOCl_2$.[116, 118, 119] Reports of the existence of SOClBr are probably incorrect.[116] Thionyl bromide decomposes slowly at room temperature ($4\,SOBr_2 \longrightarrow S_2Br_2 + 2\,SO_2 + 3\,Br_2$) and is rapidly hydrolyzed by water. Thionyl bromide converts carboxylic acids to acid bromides and substituted alcohols to the corresponding bromides.[119, 120] A general method involving conversion of alcohols to sulfites with $SOCl_2$ and cleavage of the $(RO)_2SO$ with thionyl bromide is recommended for the preparation of alkyl bromides.[121] Thionyl bromide reacts with pyridinium halides to give $C_5H_5NH^+\ XBr_2^-$ along with S and SO_2.[122, 123] Sulfur exchange between sulfur dioxide and thionyl bromide is slow[124] unless ionic halides or catalysts are present.[125, 126]

A review of the synthetic uses of sulfuryl bromide has been made.[99]

THIONYL IODIDE

Thionyl iodide, SOI_2, is unstable. Its formation by reaction of thionyl chloride in carbon tetrachloride solution with potassium iodide,[127, 128] has been reported and its decomposition was followed by spectroscopic means. It is decomposed by light. Dilute solutions in the dark are claimed to be stable for eight hours.[127] It has been considered to be an intermediate in the following reactions:[129]

(20) $(C_2H_5O)_2SO + 6\ HI \longrightarrow H_2S + 2\ C_2H_5OH + H_2O + 3\ I_2$

(21) $SOCl_2 + 6\ HI \longrightarrow H_2S + H_2O + 2\ HCl + 3\ I_2$

The results probably bear reinvestigation, since quaternary ammonium iodides, when treated with thionyl chloride, yield salts as follows:[130]

(22) $2\ I^- + 2\ SOCl_2 \longrightarrow 2\ ICl_2^- + SO_2 + S$.

Iodine is liberated when potassium iodide is added to these salts.

TABLE 1.

KNOWN SULFUR HALIDES AND SULFUR-OXYGEN-HALOGEN COMPOUNDS[1]

BINARY			TERNARY		
Fluorides	Chlorides	Bromides and Iodides	Fluorides	Chlorides	Bromides and Iodides
S_2F_2 [2]	S_2Cl_2 [7,8]	S_2Br_2 [11]	SOF_2 [13]	$SOCl_2$ [13]	$SOBr_2$ [13]
		(S_2I_2, SI_2)[12]	$SOClF$[13]	SO_2ClF[20]	(SOI_2) [13]
SF_2 [3]	SCl_2 [9]		SO_2F_2 [14]	SO_2Cl_2 [21]	SO_2BrF [24]
SF_4 [4]	SCl_4 [9]		$S_2O_5F_2$ [15]	$S_2O_5Cl_2$ [22]	(SO_2I_2) [25]
SF_6 [5]			SO_2FCl [16]	$S_3O_8Cl_2$ [23]	"Bromine and iodine sulfates"[26]
S_2F_{10}[6]	S_nCl_2 [10]	S_nBr_2 [10]	$S_2O_6F_2$ [17]		
			$S_2F_{10}O_2$ [18]		
			F_4SO [19]		
			F_5SOF [19]		
			$SO_2(OF)F$ [19]		

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