SMOKE-FORMING CHEMICALS

KIRBY E. JACKSON[1]

Department of Chemistry, Georgia School of Technology, Atlanta, Georgia

Received November 4, 1937

According to Prentiss (261) the colloidal state of matter is characterized by an intimate admixture of at least two phases,—the dispersed phase and the dispersion medium. By a dispersion of this kind is meant the regular distribution of one substance in another in such a way that the individual particles of the one substance are suspended separately from each other in the second substance. In this sense smoke is to be regarded as a two-phase colloid whose dispersion medium (the air) is in the gaseous state and whose dispersed phase is a solid or liquid. So-called colloidal solutions of this kind have physical and chemical behavior entirely different from that of normal solutions, in that the size of the particles may vary within certain limits without causing the solution to lose its colloidal character.

The particles of a smoke or fog vary in size from those just large enough to be perceived by the unaided eye to those that approach the size of a single molecule. In general, smoke particles are intermediate in size between dust particles (10^{-4} cm.) and gas particles (10^{-7} cm.) and average about 10^{-5} cm. in diameter. As a rule, the smaller the particles in a given quantity of smoke, the greater is their obscuring power; hence the aim is to generate a smoke consisting of the maximum number of particles of medium size.

Since smoke is a suspension of minute solid or liquid particles, it is not a true gas and does not follow the law of gaseous diffusion. However, owing to the collisions of the molecules of air with the smoke particles, the latter exhibit Brownian movements, as a result of which they gradually diffuse and spread. Because of their greater mass and inertia and the resistance of the air, the larger particles of smoke diffuse more slowly than the smaller ones. But, compared with the effects of wind and convection currents, diffusion plays an almost negligible part in the dispersion of smokes; even in a very dense smoke the weight of the smoke particles is only a small fraction of 1 per cent of the weight of the air it occupies, so that a smoke cloud is distinguished from the surrounding atmosphere only by the small amount of suspended foreign material.

[1] Present address: 2514 Belmont Boulevard, Nashville, Tennessee.

If smoke is released in warm air, it will rise as the warm air expands. If released in cold air, where these upward convection currents are absent, the smoke will spread out in a horizontal layer and cling to the ground. The movement of the cloud is therefore merely the movement of the air, which accounts for the characteristic behavior of smoke clouds.

Since floating smoke particles are themselves heavier than air, they gradually fall, although at a very slow rate which varies with the size of the particles. Thus, according to Grey and Patterson (120), a smoke particle having a diameter of 10^{-4} cm. falls about 0.071 in. per minute, which is so slow as to be negligible for practical purposes.

In the same manner as particles in colloidal solution, smoke particles tend to unite and increase in size by cohesion and coalescence as they come in contact with each other by Brownian movements or air currents. This agglomeration takes place much more rapidly in a dense than in a thin smoke. When the smoke particles are completely dry, agglomeration is not observed, but when the particles are liquid, or of a deliquescent solid with condensed surface moisture, this is more pronounced. The increase in the number and size of the larger at the expense of the smaller particles increases the rate of settling and decreases the concentration of the cloud. Also, the smaller smoke particles vaporize more rapidly because their surfaces are greater in proportion to their weight. Thus it follows that a smoke is most stable when the particles are of the minimum size and consist of a dry non-deliquescent solid material.

Fries and West (101) classify smokes as screening and toxic: included among the former are phosphorus, chlorosulfonic acid, oleum, sulfur trioxide, tin tetrachloride, silicon tetrachloride, and titanium tetrachloride; among the latter are methyldichloroarsine (154), phenyldichloroarsine, diphenylcyanoarsine (155), triphenylchloroarsine, diphenylchloroarsine (156), and cyanogen bromide. The smoke-forming chemicals described in this article are phenyldichloroarsine, chlorosulfonic acid, titanium tetrachloride, and silicon tetrachloride.

I. PHENYLDICHLOROARSINE, $C_6H_5AsCl_2$

Preparation

Michaelis (209) in 1875 first prepared phenyldichloroarsine by heating mercury diphenyl with excess arsenious chloride at 170°C. Since that time many modifications and new processes have been devised, as illustrated by the following methods of preparation: by warming phenylarsenious oxide with hydrochloric acid (180, 211); by passing a mixture of arsenic trichloride and benzene through a tube heated to redness (180) or by heating it for 40 hr. (179); by the decomposition of phenyltetrachloroarsine with glacial acetic acid (180); by the decomposition of diphenylchloroarsine (180); by heating diphenyltrichloroarsine in a sealed tube to 200°C. (180); by heating triphenylarsine with excess aluminum chloride under pressure to 250°C. (216); by the oxidation of phenylhydrazine with pyroarsenic acid, phenylarsenic acid, or arsenic acid in the presence of copper (372); by heating phenyl(β-ethylmercaptoethyl) arsinic acid or phenyl(β-ethylmercaptophenyl)arsinic acid with phosphorus trichloride (310); by the reduction of phenylarsenic acid (51); by the decomposition of 10-phenyl-9,10-dihydrophenarsazine (371) or of 10-phenyl-5,10-dihydrophenarsazine (2) with gaseous hydrogen chloride; by the action of thionyl chloride on phenylarsenic acid (321). By heating triphenylarsine for 3 hr. with arsenic trichloride at 250-280°C. Morgan and Vining (225) obtained phenyldichloroarsine from the fraction coming over between 150° and 190°C. Heating phenylmercuric chloride with arsenic trichloride (278), heating arsenic trichloride and benzene in the presence of aluminum chloride (172, 357) or calcium chloride, or heating phosphorus trichloride and benzene in the presence of arsenic trichloride (180) produces phenyldichloroarsine. When triphenylbismuthine (54) or triphenylstibine (53) in anhydrous ether is heated with arsenic trichloride, phenyldichloroarsine is obtained as one of the products. The reaction of triphenylarsine in anhydrous ether with antimony trichloride (53), or of triphenylbismuthine or triphenylarsine with arsenic trichloride (53), produces the chloroarsine. Phenylmethylchloroarsine, phenylmethylarsinic acid, diphenylarsinic acid, or diphenylarsenious chloride when treated with thionyl chloride (113) forms phenyldichloroarsine. Reduction of phenyl(*p*-thiocyanophenyl)arsinic acid in cold hydrochloric acid with sulfur dioxide (311) produces phenyldichloroarsine. A benzene solution of triphenylchloromethane treated with a benzene solution of phenylarsine forms phenyldichloroarsine (34). Upon heating phenylarsenic oxide with concentrated hydrochloric acid (322) phenyldichloroarsine results. When moist chlorine, cooled phosphorus pentachloride, chloral, or chloral hydrate is allowed to react with bis(α-hydroxyethyl)phenylarsine, phenyldichloroarsine is produced (245). It is also obtained by heating triphenylarsine with arsenic trichloride for 30 hr. at 250°C. (215) or by heating azobenzene with chlorine (218). By treating phenylchloroarsineacetic acid with a chloroform solution of phosphorus pentachloride, Quick and Adams (266) prepared phenyldichloroarsine; Sherlin and Yakubovich (310) obtained it by acidifying phenyl(β-ethylphenylmercapto)arsine chloride with hydrochloric acid. Oechslin (239) obtained British patent 173,796 (July 10, 1920) for the preparation of phenyldichloroarsine by heating a diarylarsine with arsenic trichloride; Pope and Turner (260) obtained British patent 142,880 (June 11, 1918) for the preparation of phenyldichloroarsine by heating triphenylarsine with arsenic trichloride for 4 hr. at 300°C.

Physical properties

Phenyldichloroarsine is a colorless, strongly refractive liquid of mildly unpleasant odor (209). It is not hydrolyzed or dissolved by water even on heating; however, it is easily dissolved by all alkalies (180).

Its boiling point has been reported as follows: 114°C. at 14 mm. (322); 117–120°C. at 7 mm. (371); 118°C. at 9 mm. (138); 124.5–125°C. at 12 mm. (126); 127°C. at 12 mm. (113); 127–130°C. at 10–11 mm. (310); 128°C. at 16 mm. (113); 153–155°C. at 18 mm. (245); the following boiling points have been found at atmospheric pressure: 249°C. (209); 250–252°C. (215); 250–255°C. (278); 252–253°C. (371); 252–255°C. (210); 254°C. (180, 212); 254.4–257.6°C. (126). The following values have been reported for the density: $d_{4°}^{17.5°}$, 1.655; $d_{4°}^{39.5°}$, 1.628; $d_{4°}^{60.5°}$, 1.601; $d_{4°}^{79.5°}$, 1.578 (138); $d_{4°}^{19°}$, 1.6516; $d_{4°}^{15.3°}$, 1.6561 (126); $d_{4°}^{24°}$ (vacuum), 1.646 (157). The molecular refraction for the D sodium line at 24°C. is 48.50 (157). Gryszkiewicz-Trochimowski and Sikorski (126) found the index of refraction at 15.3°C. to be as follows: $n_\alpha = 1.6313$; $n_D = 1.6386$; $n_\beta = 1.6575$. The values of the molecular refraction are 47.99 for the H_α line, 48.43 for the D line, and 49.56 for the H_β line.

Baxter, Bezzenberger, and Wilson (10) determined the vapor pressure of phenyldichloroarsine by the "air current" or "transference" method. A known volume of air, as determined by the measured volume of water run out of an aspirator, was saturated with the vapor of phenyldichloroarsine by passing it through a weighed receptacle maintained at constant temperature in a water thermostat. The loss in weight of the saturating tube furnished the weight of evaporated substance. From the latter quantity the volume of vapor was calculated on the assumption that the volume of a gram-molecule under standard conditions is 22.4 liters. The per cent of vapor multiplied by the interior pressure, as determined by the barometric reading and an open-arm manometer attached to the aspirator, gave the vapor pressure. The control of the temperature in the thermostat was within 0.1°C. A plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature gives a very nearly straight line, which, therefore, can be represented by an empirical equation of the form:

$$\text{log vapor pressure} = A + B/273 + t$$

Vapor pressure values calculated by means of these equations agreed with the observed values within the experimental error (see table 1). For a higher degree of accuracy the equations were not adequate, however, and can not be trusted for extrapolation over any considerable range.

Henley and Sugden (138) calculated the parachor of phenyldichloroarsine by the formula:

$$[P] = M\gamma^{\frac{1}{4}}(D - d)$$

where M = molecular weight, γ = surface tension (dynes per centimeter) determined by the method of maximum bubble pressure, and D and d are the densities of liquid and vapor, respectively, which were determined by means of a U-shaped pyknometer (see table 2).

Blicke and Smith (36) determined the molecular weight of phenyldichloroarsine by the ebullioscopic procedure in the Menzies apparatus, using benzene as solvent: (Δt°) = 0.1968; molecular weight found (A) = 234; molecular weight calculated (B) = 223; A/B = 1.05.

TABLE 1

Vapor pressure of phenyldichloroarsine

$\log$ vapor pressure $= 9.150 - 3164/273 + t$

TEMPERATURE	VAPOR PRESSURE (OBSERVED)	VAPOR PRESSURE (CALCULATED)	DIFFERENCE (CALCULATED—OBSERVED)
°C.	mm.	mm.	mm.
45	0.159	0.159	0.000
35	0.076	0.076	0.000
30	0.049	0.051	+0.002
25	0.035	0.034	−0.001
15	0.014	0.014	0.000
0	0.004	0.004	0.000

TABLE 2

Parachor of phenyldichloroarsine

TEMPERATURE	γ	D	P
°C.			
18.5	44.64	1.654	348.3
42.0	41.51	1.624	348.3
62.6	38.72	1.600	347.5
79.0	37.33	1.578	349.1
Mean value			348.3

Chemical properties

(*1*) *Heating.* When phenyldichloroarsine is passed through a red-hot tube, decomposition takes place, the products being diphenyl, arsenic trichloride, and arsenic (180).

(*2*) *Action with inorganic salts.* An absolute alcoholic solution of phenyldichloroarsine when shaken with sodium iodide forms phenyldiiodoarsine, $C_6H_5AsI_2$, lemon-yellow needles, m.p. 15°C. (49, 323) and b.p. 185°C. (323); this compound decomposes at 190°C. (49).

When phenyldichloroarsine is treated with silver cyanide there is formed crystalline phenylarsinedicyanide, $C_6H_5As(CN)_2$, which melts at 78.5–79.5°C. and possesses a feeble aromatic odor (125).

(*3*) *Action with ammonia and alkalies.* When dry ammonia is passed into an anhydrous benzene solution of phenyldichloroarsine the reaction goes on smoothly with formation of phenylarsenimide, $C_6H_5As{=}NH$, which is easily soluble in benzene and xylene but difficultly soluble in ether and absolute alcohol. It separates as beautiful flakes from absolute alcohol (212). It begins to sinter at 265°C. and melts at 270°C. (212). The nitrogen is only feebly attached to the arsenic atom, hydrolysis being readily effected by moisture. The imide is very irritating to the skin in the powder form, in the vapor of a volatile solvent, and in solution (153).

Upon boiling phenyldichloroarsine with concentrated sodium hydroxide solution (180), sodium carbonate (211), or sodium bicarbonate (49) there is formed phenylarsenious oxide, C_6H_5AsO. At ordinary temperatures it has an anise-like odor. On warming it attacks the mucous lining of the nose. It is insoluble in water, feebly soluble in cold alcohol, but easily soluble in hot alcohol and cold benzene. It melts at 119–120°C.

(*4*) *Action with mercury and lead compounds.* When mercury dibutyl and phenyldichloroarsine are allowed to react there is formed phenylbutylchloroarsine, $C_6H_5(C_4H_9)AsCl$, a clear yellow liquid, boiling at 165–166°C. at 14 mm. Its density at 0°C. is 1.35 (337).

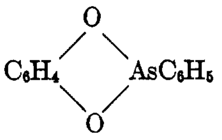
Depending upon the relative amounts of mercury diphenyl and phenyldichloroarsine used, the following compounds are formed: triphenylarsine, $(C_6H_5)_3As$; diphenylchloroarsine, $(C_6H_5)_2AsCl$; phenylmercuric chloride, C_6H_5HgCl. This is illustrated by the following equations:

$$C_6H_5AsCl_2 + 2Hg(C_6H_5)_2 \rightarrow (C_6H_5)_3As + 2HgClC_6H_5 \qquad (180)$$

$$2C_6H_5AsCl_2 + Hg(C_6H_5)_2 \rightarrow 2(C_6H_5)_2AsCl + HgCl_2 \qquad (214)$$

$$C_6H_5AsCl_2 + Hg(C_6H_5)_2 \rightarrow (C_6H_5)_2AsCl + C_6H_5HgCl \qquad (75)$$

Through the action of phenyldichloroarsine on lead pyrocatechol there is formed pyrocatechol phenylarsenite,



as a white, radiant, crystalline mass; it melts at 83°C. and boils at 197–198°C. at 15 mm. In water it decomposes to phenylarsenious oxide and pyrocatechol (211).

(*5*) *Action with sodium salts.* Phenyldichloroarsine in 10 *N* sodium hydroxide solution upon being brought in contact with an aqueous solution of sodium chloroacetate produces no immediate reaction, but within 30 min. the reaction is complete. After recrystallization from hot water the product, phenylarsenoacetic acid, $C_6H_5As(O_2H)CH_2COOH$, melts at 141–142°C. (with decomposition) (266).

An aqueous solution of sodium chloroacetoarsanilate is added to a solution of phenyldichloroarsine in 10 *N* sodium hydroxide. The chalky white material is extracted with hot water, then with hot alcohol, and finally dried at 110°C. The product, *p*-phenylarsinoacetoarsanilic acid, $C_6H_5As(O_2H)CH_2CONHC_6H_4AsO_3H_2$, does not melt below 250°C.(255).

A xylene solution of phenyldichloroarsine, reacting with a xylene solution of sodium benzoate, forms dibenzyl phenylarsenite, $C_6H_5As(OCH_2C_6H_5)_2$, a yellowish liquid having an odor like that of benzyl alcohol and boiling at 296°C. at 30 mm. Its specific gravity at 13°C. is 1.2853 (212).

When an aqueous solution of sodium *o*-chloroacetoaminobenzoate is added to phenyldichloroarsine in 10 *N* sodium hydroxide solution, the product is phenylarsino-*o*-acetoaminobenzoic acid, $C_6H_5As(O_2H)CH_2CONHC_6H_4COOH$ (*o*), m.p. 198–200°C. (with decomposition) (266).

Kharasch (166) obtained U. S. patent 1,589,599 (June 22, 1926) for the formation of the compound $C_6H_5As(SCH_2COOH)_2$, resulting from the action of an aqueous solution of a metal salt of thioglycolic acid on phenyldichloroarsine. This compound has germicidal and therapeutic properties.

(*6*) *Action with halogens and halogen compounds.* Upon direct addition of chlorine to phenyldichloroarsine, Dehn and Wilcox (74) and Michaelis (209, 210, 211) found that phenyltetrachloroarsine, $C_6H_5AsCl_4$, is formed in yellow needles, melting at 45°C. On addition of water to the tetrachloride the oxychloride, $C_6H_5AsOCl_2$, is formed; with more water phenylarsinic acid, $C_6H_5AsO(OH)_2$, is formed, which crystallizes very readily in long white needles, melting at 168°C.

p-Dibromobenzene results from the action of bromine on phenyldichloroarsine. It forms colorless monoclinic crystals, m.p. 89°C. (180, 211).

Schuster (307) found that when phenyldichloroarsine is boiled for 45 min. with fuming hydrogen bromide (density, 1.75) the yield of the bromine derivative by the replacement of the arsenic radical is not very good.

A mixture of phenyldichloroarsine, alcohol, sodium hydroxide, and methyl iodide after standing for one day was neutralized with hydrochloric acid; phenylmethyliodoarsine, $C_6H_5(CH_3)AsI$, was formed (50).

The reaction between phenyldichloroarsine in 10 *N* sodium hydroxide solution and ethylene bromide forms ethylenediphenyldiarsinic acid,

$C_2H_4(C_6H_5AsO_2H)_2$, which separates first as an oil but gradually solidifies, and upon recrystallization from hot water or alcohol melts at 209–211°C. (266).

Phenyldichloroarsine when treated with *p*-bromotoluene and finely sliced sodium in anhydrous ether forms white, rhombohedral crystals of phenylditolylarsine, $C_6H_5As(C_7H_7)_2$, m.p. 101°C. This compound is soluble in ether, chloroform, benzene, and hot alcohol, and slightly soluble in cold alcohol and glacial acetic acid (212).

Phenyldichloroarsine when treated with bromoxylene and finely divided sodium in anhydrous ether forms *m*-dixylylphenylarsine, $C_6H_5(C_6H_3(CH_3)_2)_2As$, as an oil which, on rubbing, separates as needles of the triclinic system, m.p. 99°C. This substance is soluble in most organic solvents but only slightly soluble in cold alcohol. It is refractive (213).

(*7*) *Action with hydrocarbons.* Hunt and Turner (147) found that acetylene is slowly absorbed by a solution of anhydrous aluminum chloride in phenyldichloroarsine to give, after treatment with ice and hydrochloric acid, phenyl-β-chlorovinyldichloroarsine, $AsC_6H_5ClCH{=}CHCl$, a pale yellow, unpleasant smelling liquid boiling at 140–145°C. at 10 mm., phenyl-ββ′-dichlorodivinylarsine, $AsC_6H_5(CH{=}CHCl)_2$, boiling at 155–160°C. at 10 mm., and compounds of higher boiling point. The last, which have not been investigated further, arise mainly from the intermolecular condensation of phenyldichloroarsine, a process which is preceded by the formation of a crystalline additive compound, $AsC_6H_5Cl_2 \cdot AlCl_3$. If the $C_6H_5AsCl_2 \cdot AlCl_3$ solution is not cooled during the absorption of acetylene, or if the ice–acid treatment is omitted, β-chlorovinyldichloroarsine and benzene are also formed, in accordance with equations of which the simplest is:

$$AsC_6H_5ClCH{=}CHCl + HCl \rightarrow C_6H_6 + AsCl_2CH{=}CHCl$$

A solution of anhydrous aluminum chloride in cold phenyldichloroarsine on standing for a few hours deposits the additive compound, $AsC_6H_5Cl_2 \cdot AlCl_3$, as pale yellow crystals. If the additive compound, or a freshly prepared solution of aluminum chloride in the phenyldichloroarsine, is treated with hydrochloric acid, phenyldichloroarsine is recovered unchanged, but if the solution is kept for more than a few hours a mixture of products results, with boiling points ranging from 130°C. to 270°C. at 15 mm., being higher the longer the solution stands (147).

When phenyldichloroarsine is shaken with a mixture of aluminum chloride and cyclohexane for 16 hr. at 65–70°C., it is reduced with the formation of free arsenic (233).

(*8*) *Action with sodium derivatives of alcohols and phenols.* By the action of an ethereal solution of phenyldichloroarsine on sodium methylate there is formed dimethyl phenylarsenite, $C_6H_5As(OCH_3)_2$, a colorless, characteristic smelling liquid, having a boiling point of 116°C. at 18 mm. and 220°C. at 760 mm. Its specific gravity at 20°C. is 1.343. It hydrolyzes easily in water or alkali, forming phenylarsenious oxide and methyl alcohol (212).

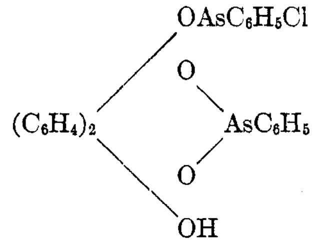
An ethereal solution of sodium ethylate acts upon phenyldichloroarsine to form diethyl phenylarsenite, $C_6H_5As(OC_2H_5)_2$, a colorless, unpleasant smelling liquid, boiling at 122°C. at 15 mm. (212). McKenzie and Wood (191) found that when an alcoholic solution of sodium ethylate was added to phenyldichloroarsine, and the mixture was heated on a water bath and distilled under diminished pressure, phenylethoxychloroarsine, $C_6H_5AsClOC_2H_5$, was obtained. This is a colorless oil, boiling at 125–126°C. at 12 mm. It gradually undergoes hydrolysis in contact with water, being transformed into a white solid which, when recrystallized from petroleum, separates in needles which melt at 127–130°C. It is curious that this product has a melting point considerably higher than that recorded in the literature for phenylarsenious oxide.

An ethereal solution of sodium phenylate in contact with phenyldichloroarsine forms diphenyl phenylarsenite, $C_6H_5As(OC_6H_5)_2$, a colorless liquid, boiling at 245°C. at 15 mm. Its specific gravity at 20°C. is 1.32 (212).

A xylene solution of phenyldichloroarsine reacts with a xylene solution of sodium tolylate forming ditolyl phenylarsenite, $C_6H_5As(OC_6H_4CH_3)_2$, a yellowish oil boiling at 285°C. at 12 mm. Its specific gravity at 13°C. is 1.2989 (212).

By the reaction of the sodium derivative of β-naphthol in ether with an ethereal solution of phenyldichloroarsine there is formed di-β-naphthyl phenylarsenite, $C_6H_5As(OC_{10}H_7)_2$, in colorless needles melting at 113–114°C.(212).

By the action of phenyldichloroarsine on sodium pyrocatecholate there is formed the chlorine-containing compound,



m.p. 63°C. (212).

(*9*) *Action with sulfides.* When hydrogen sulfide is passed into an aqueous or alcoholic solution of phenyldichloroarsine there results phenylarsinosulfide, C_6H_5AsS, a yellowish white powder; its melting point has been reported as 152°C. (177, 230, 304) and as 174–176°C. (36).

Upon treating the sodium salt resulting from the action of phenyldichloroarsine and sodium hydroxide with ethyl β-bromoethyl sulfide and oxidizing the resulting product, there is formed phenyl(β-ethylmercaptoethyl)arsinic acid, $C_6H_5As(O_2H)C_2H_4SC_2H_5$, as colorless needles or six-sided prisms, melting at 177°C. It is soluble in alcohol, acetone, carbon disulfide, and hot water, and insoluble in hydrochloric acid (310).

Phenyl(β-ethyl isoamylsulfone)arsinic acid, $C_6H_5As(O_2H)C_2H_4SO_2C_5H_{11}$, results from treating the sodium salt formed from phenyldichloroarsine and sodium hydroxide with isoamyl β-bromoethyl sulfide and oxidizing the product. It forms long colorless crystals, melting at 139.5–140.5°C. It is slightly soluble in hot water and acetone (310).

Phenyl(β-phenylsulfonylethyl)arsinic acid, $C_6H_5As(O_2H)C_2H_4SO_2C_6H_5$, results from treating the sodium salt formed from phenyldichloroarsine and sodium hydroxide with phenyl β-bromoethyl sulfide and oxidizing the product. It is obtained as long needles, melting at 192–193°C. (with slight decomposition) (310).

(*10*) *Action with zinc alkyls.* Dimethylphenarsazine, $(CH_3)_2C_6H_5As$, b.p. 200°C., is formed as the result of the reaction between zinc methyl and phenyldichloroarsine (214).

A dilute benzene or ether solution of phenyldichloroarsine added dropwise to zinc ethyl forms a colorless, highly refractive liquid of unpleasant odor, diethylphenarsazine, $(C_2H_5)_2C_6H_5As$, boiling at 240°C. (180, 211, 364).

(*11*) *Action with Grignard reagents.* Upon treating magnesium shavings in ether with methyl bromide and adding phenyldichloroarsine there is formed dimethylphenarsazine, $(CH_3)_2C_6H_5As$, b.p. 193–200°C. (323).

Phenyldichloroarsine by reacting with methylmagnesium iodide forms phenyldimethylarsine, $C_6H_5(CH_3)_2As$, b.p. 200°C. (364). Henley and Turner (139) obtained phenyltrimethylarsonium thiophenoxide by treating phenyldichloroarsine with methylmagnesium iodide. It melts at 144–145°C. It crystallizes from alcohol–ether solution in white leaflets, soluble in water or alcohol but insoluble in ether.

A Grignard reagent prepared from ethyl bromide, magnesium, and ether was treated gradually with a benzene solution of phenyldichloroarsine. After appropriate treatment there was obtained phenyldiethylarsine, $C_6H_5(C_2H_5)_2As$, a colorless oil, boiling at 111–115°C. at 14 mm. (49).

Phenyldichloroarsine reacts with *n*-propylmagnesium bromide to give phenyldipropylarsine, $C_6H_5(C_3H_7)_2As$, which boils at 125°C. at 10 mm. and at 141°C. at 19 mm. Other physical constants are: $d_{4^\circ}^{20^\circ}$, 1.1078; $n_F^{20^\circ}$, 1.5595; $n_D^{20^\circ}$, 1.59631; $n_C^{20^\circ}$, 1.5409 (159).

Phenyldichloroarsine reacts with *n*-amylmagnesium bromide to give phenyldiamylarsine, $C_6H_5(C_5H_{11})_2As$, which boils at 174°C. at 10 mm., and at 186°C. at 16 mm. (159).

Phenyldichloroarsine reacts with cyclohexylmagnesium bromide to form dicyclohexylphenylarsine, $(C_6H_{11})_2C_6H_5As$, a colorless liquid, boiling at 220°C. at 14 mm. (276, 319).

When the magnesium compound from 1,4-dibromobutane reacts with phenyldichloroarsine there is obtained cyclotetramethylenephenylarsine, $(CH_2)_4AsC_6H_5$. It is a mobile oil of faint and not unpleasant odor, b.p. 128.5°C. at 15–16 mm. It does not markedly oxidize in air at room temperature, and remains unchanged for months in the light. The following values have been reported for its density and refractive index: $d_{4^\circ}^{0^\circ}$, 1.2997; $d_{4^\circ}^{10^\circ}$, 1.2896; $d_{4^\circ}^{20^\circ}$, 1.2794; $d_{4^\circ}^{30^\circ}$, 1.2694; $d_{4^\circ}^{17^\circ}$, 1.2824; $n_D^{17^\circ}$, 1.6768; $n_F - n_C$ at 17°C., 0.02434 (123).

Reaction of the magnesium compound of 1,5-dibromopentane (or 1,5-dichloropentane) with phenyldichloroarsine (123) gives a liquid with a faint unpleasant odor, b.p. 153–154°C. at 16–20 mm. It does not markedly oxidize in the air at room temperature. Its density (20°/4°) is 1.248; $n_D^{21.4^\circ}$, 1.5944; $n_F - n_C$ at 22.4°C., 0.02167 (124).

(12) Action with arsines. Phenyldichloroarsine reacted with dimethylarsine in a sealed tube filled with carbon dioxide; no pressure was developed. The ether extract of the reaction product gave compact white crystals of dimethylarsinephenylarsine dichloride, $C_6H_5AsCl_2(CH_3)_2AsH$, which decompose rapidly when exposed to air, apparently yielding $C_6H_5AsClAs(CH_3)_2$, an oil (66).

Phenyldimethylarsine combines readily with phenyldichloroarsine to give a colorless addition product, $C_6H_5(CH_3)_2As \cdot C_6H_5AsCl_2$, which crystallizes from alcohol in colorless needles melting at 36°C. (43).

Blicke and Powers (33) and Steinkopf and Dudek (304) obtained arsenobenzene, $C_6H_5As{=}AsC_6H_5$, m.p. 209–211°C., diphenylchloroarsine, $(C_6H_5)_2AsCl$, m.p. 40–42°C., and tetraphenyldiarsyl, $(C_6H_5)_2AsAs(C_6H_5)_2$, m.p. 125–129°C., when phenyldichloroarsine was treated with diphenylarsine, as shown in the following equations:

$$4C_6H_5AsCl_2 + 4(C_6H_5)_2AsH \rightarrow 2C_6H_5As{=}AsC_6H_5 + 4(C_6H_5)_2AsCl + 4HCl$$

$$2C_6H_5AsCl_2 + 4(C_6H_5)_2AsH \rightarrow C_6H_5As{=}AsC_6H_5 + 2(C_6H_5)_2AsAs(C_6H_5)_2 + 4HCl$$

Steinkopf and Smie (310), by condensing phenyldichloroarsine with diphenylarsine, obtained triphenylchlorodiarsine, $(C_6H_5)_2AsAsC_6H_5Cl$, white needles, m.p. 164°C.:

$$C_6H_5AsCl_2 + (C_6H_5)_2AsH \rightarrow (C_6H_5)_2AsAsC_6H_5Cl + HCl$$

When phenyldichloroarsine was mixed with an equal weight of bis(α-hydroxyethyl)phenylarsine a slight warming and turbidity was observed, and after one week the mixture was practically solid. The product, after washing, proved to be arsenobenzene, $C_6H_5As{=}AsC_6H_5$, m.p. 196–199°C. (230).

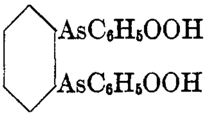
The products resulting from the reaction between tetraphenyldiarsyl and phenyldichloroarsine are arsenobenzene and diphenylchloroarsine (33):

$$2(C_6H_5)AsAs(C_6H_5)_2 + 2C_6H_5AsCl_2 \rightarrow C_6H_5As{=}AsC_6H_5 + 4(C_6H_5)_2AsCl$$

(*13*) *Action with acids.* Phenyldichloroarsine reacts with chlorosulfonic acid forming benzenesulfonyl chloride, $C_6H_5SO_2Cl$, an oil which crystallizes with difficulty; the crystals melt at 14.5°C. (320).

When a neutral solution of diazotized anthranilic acid is condensed with an alkaline solution of phenyldichloroarsine and reduced with sulfur dioxide at 80°C. there is formed *o*-carboxydiphenylchloroarsine, a white, crystalline compound melting at 163°C. It is readily soluble in alcohol, and moderately soluble in hot benzene (3).

When *o*-aminodiphenylarsonic acid is diazotized and treated with phenyldichloroarsine in 5 *N* sodium hydroxide solution, the product is phenylene-1,2-diphenylarsonic acid

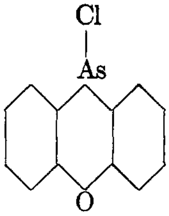


It forms pale yellow microscopic crystals, which do not melt below 310°C. It is insoluble in water and the usual organic solvents (197).

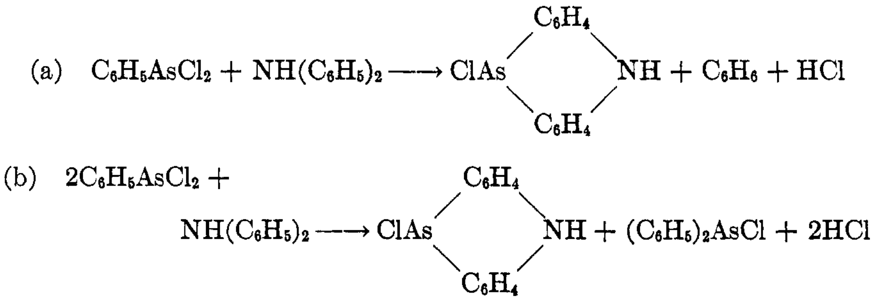
(*14*) *Action with acid chlorides.* Acetophenone results from the reaction between phenyldichloroarsine and acetyl chloride (191).

Gibson, Johnson, and Vining (114) and Malinovskiĭ (191) found that phenyldichloroarsine was dearsenicated when treated with aluminum chloride and chloroacetyl chloride in carbon disulfide, the product being ω-chloroacetophenone, m.p. 52–55°C., b.p. 130–132° at 22 mm.

(*15*) *Action with miscellaneous substances.* Upon condensation of diphenyl ether with phenyldichloroarsine in the presence of aluminum chloride (2) there is obtained 10-chlorophenoxarsine.



Burton and Gibson (51) prepared 10-chloro-5,10-dihydrophenarsazine by heating phenyldichloroarsine with diphenylarsine in the presence of *o*-dichlorobenzene:



$$\text{(a)}\quad C_6H_5AsCl_2 + NH(C_6H_5)_2 \longrightarrow ClAs\begin{matrix} C_6H_4 \\ \\ C_6H_4 \end{matrix}NH + C_6H_6 + HCl$$

$$\text{(b)}\quad 2C_6H_5AsCl_2 + NH(C_6H_5)_2 \longrightarrow ClAs\begin{matrix} C_6H_4 \\ \\ C_6H_4 \end{matrix}NH + (C_6H_5)_2AsCl + 2HCl$$

The product forms yellow needles melting at 189–190°C.

Upon boiling phenyldichloroarsine for 16 hr. with (*a*) phenyl-*p*-tolylamine, (*b*) di-*p*-tolylamine, (*c*) phenyl-α-naphthylamine there is formed (*a*) 10-chloro-2-methyl-5,10-dihydrophenarsazine, m.p. 199–200°C. (decomposition), (*b*) 10-chloro-2,8-dihydrophenarsazine, m.p. 261–262°C., and (*c*) *N*-chloro-7,12-dihydrobenzophenarsazine, m.p. 218–219°C.

Chloroacetanilide when added to a solution of phenyldichloroarsine in 10 *N* sodium hydroxide produces phenylarsinoacetanilide, $C_6H_5As(O_2H)$-$CH_2CONHC_6H_5$, which crystallizes from water in small needles, m.p. 182–183°C. (decomposition) (266).

Phenyldichloroarsine in 10 *N* sodium hydroxide solution reacting with chloroacetophenetidine forms phenylarsinoacetophenetidine, $C_6H_5As(O_2H)$-$CH_2CONHC_6H_4OC_2H_5$ (*p*), which crystallizes from alcohol in needles, m.p. 175°C. (decomposition) (266).

Reaction between β-phenoxyethyl bromide and phenyldichloroarsine in 10 *N* sodium hydroxide solution forms β-phenoxyethylphenylarsinic acid, $C_6H_5As(O_2H)CH_2CH_2OC_6H_5$, which separates first as an oil but soon crystallizes; it melts at 122–123°C. (266).

Addition of an alcoholic solution of chloropicrin dropwise to an alcoholic solution of the sodium salt of phenyldichloroarsine gives phenylarsinic acid, m.p. 158–159°C. (369).

Physiological action

LaCoste and Michael (180) found phenyldichloroarsine violently corrosive to the skin. In contact with the skin of dogs it produces hyperemia, swelling, edema, ulceration, necrosis, etc.; it produces similar changes, together with vesication, on human skin (134). Flury (96) found that intense cell poisoning is caused by phenyldichloroarsine when cells are in contact with it either in stable fluid form or as a gas. Plant cells are similarly affected. It differs from strong caustics in that it produces marked inflammatory reactions and necrosis in the lowest concentrations. The irritant action upon sensory nerves is quite pronounced. The irritating effect is not due to the splitting off of acids or to the action of hydrogen ions. Gilchrist and Matz (116) found that the physiological action of the arsenicals consists in congestion of the mucous membrane of the nose, throat, and bronchi, and edema of the lungs. Occasionally motor and sensory nerve changes are observed, from which recovery is rapid and uniform. Fegler (94) observed that when phenyldichloroarsine in the form of lecithin emulsions was intraveneously injected into dogs in doses of 3 mg. per kilogram of weight a violent apnea and a sudden drop in blood pressure occurred; after vagotomy, however, it had no effect on blood pressure or respiration.

Test

According to Blicke and Oakdale (33) the following experiment illustrates the serviceability of the piperidine salt of dithiocarbamic acid as a reagent for the identification of a small quantity of phenyldichloroarsine. To one drop (0.0306 g.) of the latter compound there was added 0.127 g. (five times the calculated amount) of the piperidine salt dissolved in about 3 cc. of dry benzene. The mixture was protected from moisture, and after 12 hr. the benzene was allowed to evaporate. The crystalline residue was washed with water until the piperidine chloride and excess piperidine salt of dithiocarbamic acid had been completely removed. The crude product weighed 0.022 g. After recrystallization from ethyl acetate the product melted at 173–174°C.

Nametkin and Nekrasov (230) found that when 1 cc. of a 0.1 per cent aqueous solution of phenyldichloroarsine was treated with two to three drops of saturated hydrogen sulfide water a distinct turbidity was formed (due to C_6H_5AsS). The test was less satisfactory in alcoholic solutions. Solutions of mercurous nitrate in phenyldichloroarsine did not oxidize the arsenic compound even after long standing, but if the solution was heated, oxidation was brought about and free mercury was formed.

Fleury (95) devised a method for the determination of phenyldichloroarsine in a mixture of other phenyl derivatives of arsenious acid. This method is dependent upon the degree of oxidation by iodine.

Uses

Schmidt, Steindorff, Fluss, and Schaffrath (301) used phenyldichloroarsine for treating seed grain for parasites.

U. S. patent 1,686,582 (October 9, 1928) was issued to Stoltzenberg (329) for the use of phenyldichloroarsine in destruction of *Opuntia* by action as vapor or spray or by injection of a 5 per cent solution in cresol or sulfuric acid. Steindorff and Schwabe (317) obtained German patent 493,147 (June 26, 1930) for the treatment of grain with phenyldichloroarsine and other arsenic compounds. Walker (350) obtained U. S. patent 1,758,958 (May 20, 1930) for a compound suitable for combating marine borers; it comprises a petroleum oil containing an arsenical compound (phenyldichloroarsine) which is toxic to marine borers and has a solubility of 0.7 to 60 parts in 100,000 parts of sea water at 20°C.

II. CHLOROSULFONIC ACID, $ClSO_2OH$

In 1854 A. W. Williamson (360) defined, if he did not discover, chlorosulfonic acid, $ClSO_3H$ or $ClSO_2OH$. It attracted some attention at that time because of the old theory of types, as it was the first example of a mixed type—the water type and the hydrochloric acid type—with the bivalent SO_2 radical. The name "chlorohydrines" was applied to combinations of this mixed type, so that chlorosulfonic acid is also called sulfuric chlorohydrin; it has also been called chlorohydrated sulfuric acid and chlorohydrosulfurous acid.

Preparation

Williamson prepared chlorosulfonic acid by the direct action of hydrochloric acid on sulfur trioxide (362) and by passing a vigorous stream of hydrogen chloride into fuming sulfuric acid (370). Beckurtz and Otto (13), Claesson (55, 56), Michaelis and Schifferdecker (217), Müller (227), Briggs (44), Behrend (16, 17), Pytasz and Rabek (265), Bert (23), and Sanger and Riegel (293, 294) obtained chlorosulfonic acid in a similar manner. Müller (227) also prepared the acid by distilling fuming sulfuric acid with phosphorus pentoxide in a current of hydrogen chloride. Williamson (362, 363), Williams (358, 360), Dewar and Cranston (79, 80), Baumstark (9), and Michaelis (206, 207) obtained chlorosulfonic acid by the action of phosphorus trichloride, phosphorus pentachloride, or phosphoryl chloride on concentrated sulfuric acid; Thorpe (335) heated a mixture of phosphoryl chloride and concentrated sulfuric acid. Williamson (362, 363) obtained chlorosulfonic acid by the action of chlorine on sulfur chloride or concentrated sulfuric acid; Moureu (226) by the action of sulfuric acid on thionyl chloride; Odling (235), Thomsen (332), and Carrara (52) by the action of moisture on sulfuryl chloride; Michaelis (208) by the action of a little water or concentrated sulfuric acid on sulfuryl chloride; Billitz and Heumann (29) and Ogier (239) by the action of water on pyrosulfuryl chloride; Railton (267) and Odling (257) by the action of imperfectly dried chlorine on moist sulfur dioxide in the presence of platinum black at red heat. Ogier (239) prepared chlorosulfonic acid by the action of gaseous hydrogen chloride on solid sulfur dioxide. Michaelis (208) prepared it from fuming sulfuric acid by the action of phosphorus oxychloride; Geuther (112) by the action of phosphorus trichloride; Thomsen (332) and Carrara (52) by the action of sulfuryl chloride; Sanger and Riegel (293) by the action of pyrosulfuryl chloride; Billitz and Heumann (29) by the action of sulfur oxytetrachloride. Beckurtz and Otto (13), Behrend (16), Müller (227), and Williams (358) obtained chlorosulfonic acid by the action of concentrated sulfuric acid on sulfur monochloride. Lepin (184) and Erdmann (90) obtained the acid by the action of carbon tetrachloride on fuming sulfuric acid. Even chlorine alone will act on sulfuric acid giving chlorosulfonic acid (13, 16, 227, 358). Melsens (202) produced chlorosulfonic acid by passing sulfur dioxide and chlorine into glacial acetic acid or by using charcoal as a catalyst.

The Société pour l'Industrie Chimique à Bale (313) obtained British patent 393,546 (June 8, 1933) for the preparation of chlorosulfonic acid by causing sulfur and chlorine, or a sulfur chloride, if necessary, in the presence of chlorine, to act upon a mixture of sulfuric acid and sulfur trioxide. Krummenacher (178) obtained U. S. patent 1,898,879 (February 21, 1932), French patent 740,944 (August 8, 1932), a British patent (December 8, 1932), and German patent 574,001 (April 7, 1933) for the preparation of the acid by causing one equivalent proportion of a metal chloride, such as sodium chloride, to react with a solution of approximately 2 moles of sulfur trioxide in approximately 1 mole of sulfuric acid. Dachlauer (67) obtained German patent 543,758 (May 25, 1929) for the preparation of the acid by uniting sulfur trioxide with hydrogen chloride at a temperature between 70° and 100°C. McKee and Salls (200) obtained U. S. patent 1,554,870 (September 22, 1924) for the preparation of chlorosulfonic acid by heating sulfuryl chloride and sulfuric acid in the presence of a mercury compound or of salts of antimony, tin, or bismuth. Briggs (44) obtained U. S. patent 1,422,335 (July 11, 1921) for a process of manufacture of chlorosulfonic acid, using contact sulfuric gas and dry hydrogen chloride. Schedler and Marchant (298) obtained British patent 131,024 (March 25, 1918) for the preparation of the acid by passing hydrogen chloride obtained as a by-product in the chlorination of organic compounds such as benzene, toluene, etc. into sulfuric acid containing about 80 per cent sulfur trioxide. The Sankyô Joint Stock Company (296) obtained Japanese patent 31,580 (October 4, 1917) for the preparation of chlorosulfonic acid by passing chlorine into concentrated sulfuric acid in the presence of sulfur or sulfur monochloride or of substances which yield them by the action of chlorine. Klages and Vollberg (168) obtained U. S. patent 613,181 (January 2, 1912) for the making of chlorosulfonic acid. Saccharin-Fabrik Aktiengesellschaft vorm Fahlberg, List & Co. (290) obtained German patent 228,424 (September 5, 1907) and British patent 16,518 (July 11, 1910) (291) for the manufacture of chlorosulfonic acid by allowing hydrogen chloride gas to act on a solution of sulfur trioxide or by simultaneously leading hydrogen chloride gas and gaseous sulfur trioxide into chlorosulfonic acid.

Physical properties

Chlorosulfonic acid is a colorless, fuming liquid of sharp, unpleasant odor. Its boiling point has been reported as follows: 60–64°C. at 2.4 mm. (294); 74–75°C. at 19 mm. (293); 78°C. at 21–22 mm. (348); 145°C. at 760 mm. (362); 150–151°C. at 775 mm. (348); 150.7–152.7°C. at 760 mm. (13); 151–152°C. at 765 mm. (293, 294); 153.3–153.6°C. at 760 mm. (335); 156°C. at 760 mm. (265); 158.4°C. at 760 mm. (208). Clausnizer (58) found that the boiling point is reduced by 1°C. when the pressure is reduced by 20.6 mm. Chlorosulfonic acid melts at $-81°$ to $-80°$C. (293, 294).

The specific gravity of chlorosulfonic acid has been reported as follows: 1.784 at 4°C. (293, 294); 1.7874 at 4°C. (335); 1.7875 at 25°C. (348); 1.776 at 18°C. (208); 1.753 (293,294); and 1.5487 at 155.3°C. (335). Baumstark (9) determined the vapor density as 4.08–4.12, the calculated value being 4.04 at 216°C.; Heumann and Kochlin (140) found the vapor density to be 2.39–2.42 at 184.4°C., 2.09 at 444°C., and 2.40 at 180–216°C. (141); Ogier (239) determined the vapor density as 2.36–2.46 between 180°C. and 216°C. Ogier gave 0.282 for the specific heat of chlorosulfonic acid between 15°C. and 80°C., 12.8 cal. for its heat of vaporization, and 40.3 cal. for its heat of solution in water. Meyer (205) and Matossi and Aderhold (195), using the k-line ($\lambda = 5460$ Å.) of the mercury spectrum in determining the Raman frequencies of sulfur in chlorosulfonic acid found them to be as follows: 194, 300, 410, 498, 606, 920, 1183, 1430. Walden found that chlorosulfonic acid has low ionizing power: $\lambda = 0.160 \times 10^{-13}$ at 25°C.

Thorpe (335) made observations of the rate of expansion of chlorosulfonic acid in a dilatometer when heated in a water bath (see table 3). The values gave the formula:

$$V = 1 + 0.00090505t + 0.00000018747t^2 + 0.000000002394t^3$$

Assuming that this formula may be taken to represent the expansion of chlorosulfonic acid from 0°C. to its boiling point, table 4 gives the relative volume at every 5° between 0° and 160°C.

Lutschinsky (190) using Batschinsky's formula, $\eta = c/v - \omega$, where η is the viscosity, v is the specific volume, and ω is a constant for the given liquid, has confirmed it for chlorosulfonic acid, c being 0.000698 and ω being 0.5440 (see table 5).

TABLE 3

Rate of expansion of chlorosulfonic acid

Δ	OBSERVED	CALCULATED	Δ	OBSERVED	CALCULATED
10.93	3377.2	3377.7	64.42	3538.3	3538.5
25.34	3420.8	3420.5	73.90	3567.5	3567.9
36.64	3454.4	3454.2	89.05	3615.6	3615.7
48.51	3489.6	3489.9	100.05	3650.7	3651.1

TABLE 4

Relative volumes of chlorosulfonic acid

t	VOLUME	*t*	VOLUME	*t*	VOLUME	*t*	VOLUME
°*C.*		°*C.*		°*C.*		°*C.*	
0	1.00000	40	1.03655	85	1.07926	130	1.12492
5	1.00453	45	1.04118	90	1.08416	135	1.13024
10	1.00906	50	1.04585	95	1.08910	140	1.13560
15	1.01361	55	1.05053	100	1.09409	145	1.14103
20	1.01817	60	1.05525	105	1.09911	150	1.14651
25	1.02274	65	1.05999	110	1.10418	155	1.15205
30	1.02732	70	1.06476	115	1.10929	160	1.15765
35	1.03193	75	1.06956	120	1.11445	155.3	1.15238
		80	1.07439	125	1.11966		

Equilibria involving chlorosulfonic acid

At 170°C. the reaction,

$$2ClSO_3H \rightleftharpoons SO_2Cl_2 + H_2SO_4$$

is a reversible one, and after 72 hr. the equilibrium mixture contains 1 mole of SO_2Cl_2, 1 mole of H_2SO_4, and 2.5 moles of $ClSO_3H$. Sulfur dioxide and chlorine are not formed between 170° and 190°C., although at a higher temperature they begin to be noticeable. Obviously, therefore, the sulfuryl chloride is not formed by the union of sulfur dioxide and chlorine, initially produced by complete dissociation of the chlorosulfonic acid, but is a direct decomposition product; this is emphasized by the fact that, when the formation of the sulfuryl chloride occurs at the boiling point of the chlorosulfonic acid, owing to the presence of a catalytic agent, its amount is not increased by the passage of a current of chlorine and sulfur dioxide through the liquid. The production of sulfur dioxide and chlorine at a high temperature is due to decomposition in the sense of the equation (284):

$$SO_3 + 2HCl \rightarrow SO_2 + H_2O + Cl_2$$

With methyl sulfate, the simplest equation is

$$2ClSO_2OH + (CH_3)_2SO_4 \rightarrow 2ClSO_2OCH_3 + H_2SO_4$$

TABLE 5

Viscosity of chlorosulfonic acid

t	η	t	η	t	η	t	η
°C.		°C.		°C.		°C.	
−10	0.0563	10	0.0329	26	0.0239	42	0.0185
−5	0.0493	12	0.0316	28	0.0230	44	0.0179
−2	0.0454	14	0.0302	30	0.0223	46	0.0174
0	0.0424	16	0.0289	32	0.0215	48	0.0169
2	0.0401	18	0.0276	34	0.0209	50	0.0166
4	0.0383	20	0.0266	36	0.0203	55	0.0158
6	0.0364	22	0.0257	38	0.0196	60	0.0151
8	0.0347	24	0.0248	40	0.0189		

but the reaction is actually more complicated and does not go quantitatively as indicated in the equation (186). In sealed tubes at room temperature an equimolar mixture reacts according to the equation

$$(CH_3)_2SO_4 + ClSO_2OH \rightarrow ClSO_2OCH_3 + HOSO_2OCH_3$$

Equilibrium is reached in about one month, and the mixture then contains 1 mole of each product to 2 moles of each of the initial substances. The ratio of $ClSO_2OCH_3$ formed to that which would be formed if the reaction were not reversible (r) = 0.36. If one of the initial substances is employed in 80 per cent excess, $r = 0.07$ after 27 hr., and 0.25 after 108 hr.; at 30°C. after 62 hr., $r = 0.09$; at 40°C. after 80 hr., $r = 0.36$. After a certain period acidity increases as a result of the reaction

$$HOSO_2OCH_3 + ClSO_2OH \rightleftharpoons ClSO_2OCH_3 + H_2SO_4$$

At room temperature this reaction is incomplete after 138 hr., but its velocity increases rapidly with temperature; after 20 hr. the same final state is reached whether at 70°C. or at 100°C. The ratio $r = 0.54$, and about 5 per cent of sulfuric acid is formed. Upon distillation under reduced pressure of the mixture of sulfate and chlorosulfonic acid about 50 per cent of the methyl chlorosulfonate is recovered, the chlorosulfonic acid is practically all lost, and sulfuric acid accumulates up to 20 per cent (41).

Chemical properties

(*1*) *Heating.* Upon heating chlorosulfonic acid in a sealed tube to 170–180°C., decomposition takes place as follows (13):

$$2ClSO_2OH \rightarrow Cl_2 + SO_2 + H_2SO_4$$

(*2*) *Action with elements.* Chlorosulfonic acid does not react with sulfur in the cold, but on warming a brisk reaction takes place, with the production of sulfur dioxide, hydrogen chloride, and sulfur dichloride. With phosphorus a violent reaction takes place, not infrequently accompanied by an explosion when the chlorosulfonic acid is warmed; sulfur dioxide and hydrogen chloride are given off. With amorphous phosphorus the action is quieter; the products are phosphorus oxychloride and phosphoric acid. Chlorosulfonic acid reacts with finely powdered arsenic with evolution of sulfur dioxide; arsenic trichloride distills off and arsenious oxide remains behind. Antimony behaves in a similar manner. Tin acts in the cold with production of tin tetrachloride in theoretical quantity according to the equation:

$$4ClSO_2OH + Sn \rightarrow SnCl_4 + 2SO_2 + H_2SO_4$$

When chlorosulfonic acid is heated with charcoal it is decomposed, with evolution of sulfur dioxide, hydrogen chloride, and carbon dioxide. Chlorosulfonic acid acts as a chlorinating agent with sulfur, arsenic, antimony, and tin (140).

(*3*) *Action with salts.* Thorpe (336) found that chlorosulfonic acid acts with great violence on silver nitrate, forming silver chloride and nitroxychlorosulfonate, $NO—O—SO_2—Cl$.

By the action of chlorosulfonic acid on potassium chromate Heumann and Koechlin (141) obtained chromyl chloride.

Chlorine is evolved when a small quantity of fused potassium nitrate is treated with chlorosulfonic acid. Subsequently, on applying heat, nitrogen peroxide is given off in large quantity. No other substances save these two could be detected, even when considerable quantities of the materials were employed in equivalent proportions, and the evolved vapors were passed through a condenser cooled to $-18°C$. At first chlorine alone escaped and no liquid condensed, but on the application of heat red vapors were formed, which, on passing into the condenser, gave a small quantity of a deep red liquid,—a solution of chlorine in nitrogen peroxide. The issuing gas on being passed into hot water gave chlorine; with cold water hydrogen chloride was produced, owing to the oxidation of the chlorine of the nitrous acid formed by the solution of the peroxide in water (359).

Upon treating sodium acetate with chlorosulfonic acid in a little acetic anhydride there is formed acetic anhydride (265).

Ruff (284) found that sodium chloride dissolves in chlorosulfonic acid with evolution of hydrogen chloride and production of the sodium salt, $ClSO_3Na$, which is precipitated by the addition of sulfuryl chloride and is readily decomposed by water.

Mercuric salts rapidly decompose chlorosulfonic acid at its boiling point into sulfuryl chloride and sulfuric acid; several other salts effect a similar result, only more slowly. The figures after the names of the following salts indicate the number of grams of sulfuryl chloride formed by boiling 50 g. of the acid for 1 hr. with 1 g. of the salt. Mercuric chloride, 13.0; mercuric sulfate, 13.0; antimony pentachloride, 7.5; antimony trichloride, 7.5; stannic chloride, 5.8; bismuth chloride, 3.3; platinic chloride, 2.5; uranyl chloride, 1.7; gold chloride, 1.2; copper sulfate, 0.8; tungsten chloride, 0.8; lead chloride, 0.7; cobalt sulfate, 0.5; magnesium chloride, 0.5. The chlorides of zinc, aluminum, iron, calcium, and sodium are without action. As the whole of the chlorosulfonic acid is easily decomposed by boiling with mercuric chloride, the method is probably capable of commercial application for the manufacture of sulfuryl chloride. The mercuric chloride is not changed at all in the action, but the sulfate is converted into mercuric chloride (284).

(*4*) *Action with oxides and chlorides.* When chlorosulfonic acid was treated with a dehydrating agent such as phosphorus pentoxide, Ogier (239) obtained pyrosulfuryl chloride, $(ClSO_2)_2O_2$.

By heating chlorosulfonic acid with phosphorus pentachloride pyrosulfuryl chloride is formed (208).

On cooling a warm solution of titanium, antimony, or selenium tetrachlorides in chlorosulfonic acid there is formed the corresponding sulfotetrachloride. Sulfoantimony oxypentachloride, $ClSO_2OSbCl_4$, boils at 150–151°C. at 726 mm.; the boiling point falls 1°C. with a decrease in pressure of 20.6 mm (60). Sulfotitanium oxytetrachloride, $ClSO_2OTiCl_3$, when dried at 100°C., is an amorphous powder. It is soluble in water with evolution of chlorine and sulfur dioxide. It fumes on exposure to damp air, and is converted into a moist white mass which is no longer soluble in water (60). Sulfoselenium oxytetrachloride, $ClSO_2OSeCl_3$, is deposited in groups of needle-shaped crystals which melt at 165°C. and boil at 183°C.; it is very deliquescent (56, 60).

Selenium oxide reacting with chlorosulfonic acid forms selenium oxychloride and pyrosulfuric acid (58). The oxychloride reacting with chlorosulfonic acid forms selenium tetrachloride and pyrosulfuric acid (58).

(*5*) *Action with hydrocarbons.* Ethylene is readily absorbed by chlorosulfonic acid yielding a colorless liquid, ethyl chlorosulfonate, boiling at 93–95°C. at 100 mm. Its vapor possesses a pungent odor and produces a copious flow of tears. Ethyl chlorosulfonate is heavier than water. It fumes when exposed to the air. It is decomposed by water slowly in the cold and rapidly when heated, with formation of hydrogen chloride, sulfuric acid, and ethyl alcohol. Hot aqueous potassium hydroxide and cold alcoholic potassium hydroxide solutions readily decompose it, ethyl chloride being evolved. It dissociates without decomposition in pure ether, but with ethyl (or amyl) alcohol it evolves ethyl chloride and ethylsulfuric acid (or amylsulfuric acid) (227).

Chlorosulfonic acid is used as a catalyst in the polymerization of cyclopentadiene. The reaction takes place violently with the formation of phenylsulfonic acid (316).

When *n*-hexane and isohexane were treated with equal volumes of chlorosulfonic acid, the isohexane became warm and in a few minutes bubbles of hydrogen chloride were rapidly evolved; the normal hexane did not rise perceptibly in temperature, and it was only after some time that hydrogen chloride was given off. Heptane and octane were similarly treated, and similar results were obtained.

The results obtained are sufficient to show that chlorosulfonic acid in the cold, like fuming nitric acid at higher temperatures, acts far less energetically on the normal paraffins than on the isoparaffins, and also less energetically on the polymethylenes than on their methyl derivatives. Generally chlorosulfonic acid acts more energetically on hydrocarbons that contain a $\equiv CH$ group than on others (363).

Benzene, treated with 10 parts of chlorosulfonic acid at 150–160°C. for 2 hr., gives *m*-benzenedisulfonyl chloride, *m*-$C_6H_4(SO_2Cl)_2$, and diphenylsulfonedisulfonyl chloride, melting at 174–175°C., together with a small amount of *p*-benzenedisulfonyl chloride, *p*-$C_6H_4(SO_2Cl)_2$. When 4 parts of benzene and 3 parts of the acid are heated to boiling for 10 min., then 40 parts of the acid are added and the mixture heated to 150–160°C. for 5 hr., diphenylsulfonedisulfonyl chloride is formed. Benzene, when heated with 40 parts of chlorosulfonic acid for 7 hr. at 140–150°C., gives diphenylsulfonyl chloride (257).

Armstrong (5) found that when chlorosulfonic acid reacts with benzene the chief products are sulfobenzide, sulfobenzoic chloride, and sulfobenzolic acid, as shown in the following equations:

$$2C_6H_6 + ClSO_2OH \rightarrow (C_6H_5)_2SO_2 + H_2O + HCl$$

$$C_6H_6 + ClSO_2OH \rightarrow ClSO_2C_6H_5 + H_2O$$

$$C_6H_6 + ClSO_2OH \rightarrow C_6H_5SO_2OH + HCl$$

Toluene and 8 parts of chlorosulfonic acid, when heated for 5 hr. at 140–150°C., give 2,4-$(ClO_2S)_2C_6H_3CH_3$, m.p. 52°C. Toluene, treated with a molecular amount of chlorosulfonic acid and heated for a short time, then treated with a large excess of chlorosulfonic acid and heated for 5 to 6 hr. at 150–160°C., gives di(*p*-methylphenyl-*m*-sulfonyl chloride) sulfone, m.p. 177–178°C. (257). The action of chlorosulfonic acid upon toluene at low temperatures (−35° to −40°C.) gives a very small yield of a mixture containing from 53 to 58 per cent of the *p*-isomer. If the mixture is made at −40°C. and then allowed to warm to 5–10°C., the yield is increased, while the per cent of the *p*-isomer is about 52 per cent. As the temperature rises the per cent of the *p*-isomer increases (−15°C., 57.5 per cent; 5–10°C., 73 per cent; 20–25°C., 76.5 per cent; 35–40°C., 86 per cent; 75–80°C., 94.5 per cent). When these facts are considered in connection with the further fact that with 1 mole of chlorosulfonic acid the main product is the acid, but with an excess of chlorosulfonic acid the main product is the chloride, it appears that the reaction takes place in two steps, and that it is essential in obtaining good yields of the chloride to allow the mixture to stand a sufficient length of time to complete the second reaction. This is important, since incomplete investigations show that the acids are not proportionately converted into the acid chlorides in dilute solutions of chlorosulfonic acid, but that the predominating acid is more quickly transformed. Any local excess of toluene should be avoided if the *o*-isomer is required in maximum yield. This is met by spraying the toluene into the acid. There is an early limit to the effect of temperature on the yield of the *o*-isomer, as is seen in the fact that the yield is lower at −40°C. than at 5–10°C. (141).

When 1 mole of the acid to 1 mole of the hydrocarbon was used, the products of the reaction were sulfotoluide, *p*-toluenesulfonyl chloride, and *p*-toluenesulfonic acid, the latter occurring in largest quantity. Since sulfotoluide results from the reaction of 1 mole of the acid and 2 moles of toluene, the presence of some undecomposed chlorosulfonic acid, also observed in the product of the reaction, is accounted for. Toluenesulfonic acid being the chief product, the essential reaction would appear to be that indicated as follows:

$$ClSO_2OH + RH \rightarrow RSO_2OH + HCl$$

At the same time the formation of this compound may be explained from the decomposition of toluenesulfonyl chloride by water, indirectly, therefore, according to the equation:

$$ClSO_2OH + RH \rightarrow RSO_2Cl + H_2O$$

The proof that such is actually the case was afforded by a second experiment, in which the reaction was allowed to proceed in the presence of phosphorus pentoxide; the quantity of the sulfonyl chloride was thereby much increased. It is therefore concluded that in the case of toluene both of the decompositions represented by the two equations given above occur, and to a like extent; the reaction indicated below also occurs, but only to a very limited extent (14):

$$ClSO_2OH + 2RH \rightarrow R_2SO_2 + HCl + H_2O$$

It was found by Holleman and Caland (80) that the action of chlorosulfonic acid on toluene forms *p*-toluenesulfonic acid, $CH_3C_6H_4SO_3H$.

o-Xylene and chlorosulfonic acid heated for 5 hr. at 150–160°C. gave 1,2,3,5-$(CH_3)_2C_6H_2(SO_2Cl)_2$ melting at 79°C.; *m*-xylene and chlorosulfonic acid gave di-*m*-xylyl sulfone, m.p. 121°C.; *p*-xylene also gave a sulfone, di-*p*-xylyl sulfone, m.p. 142°C. (257).

When naphthylene was heated with chlorosulfonic acid at 180°C. for 10 hr., tetrachlorophthalic anhydride, m.p. 255°C., was formed (351).

Corbellini (63) found chlorosulfonic acid to behave with naphthalene as a chlorosulfonating agent. When solid naphthalene was treated at 15–45°C. with chlorosulfonic acid (2 moles), 1,5-$C_{10}H_6(SO_3H)_2$ was formed, together with varying proportions of the corresponding disulfonyl chloride. When carbon tetrachloride was used as a diluent and the hydrocarbon (1 mole) was treated with either 2 or 4 moles of the acid, sulfonyl chlorides were always formed in addition to the mono- and the di-sulfonic acids. In all cases the hydrocarbon was attacked only in the 1- and 5-positions. It is probable that the first phase of the reaction consists in the formation of the sulfonic acid, which then passes to the chloride,

$$C_{10}H_7SO_3H + ClSO_2OH \rightarrow H_2SO_4 + C_{10}H_7SO_2Cl$$

these changes being accompanied by the secondary reactions,

$$C_{10}H_8 + H_2SO_4 \rightarrow C_{10}H_7SO_3H + H_2O$$

and

$$ClSO_2OH + H_2O \rightarrow H_2SO_4 + HCl$$

The final yields of the various products evidently depend on the velocities of these different reactions, these being governed by the conditions employed. The sulfochlorinating action is favored by low temperatures.

When the reaction was prolonged it continued with the formation of other products. Naphthalene was added slowly to chlorosulfonic acid at 5–10°C. (abundant evolution of hydrogen chloride), the mixture allowed to stand for 120–140 hr. at 50–55°C. (sulfur dioxide evolved), and then poured on ice; the precipitate was washed with water by decantation, and then filtered, and the residue was recrystallized from benzene. The product was 1,5-naphthalenedisulfonyl chloride, 1,5-$C_{10}H_6(SO_2Cl)_2$, m.p. 183°C. With a greater excess of chlorosulfonic acid at elevated temperature the reaction proceeded more rapidly and the yield was higher (65). Naphthalene and 10 parts of chlorosulfonic acid, acting a short time at 0°C., gave the disulfonyl chloride, m.p. 183°C. (257).

Diphenyl and 5 parts of chlorosulfonic acid, heated at 50°C. for 12 hr., gave diphenylmonosulfonic acid, m.p. 138°C.; the hydrocarbon and acid in the same ratio at 18°C. for 24 hr. gave *o′,o′*-biphenylenesulfone-*p,p′*-disulfonyl chloride, m.p. 236°C. (257).

When a slight excess of an aqueous solution of chlorosulfonic acid was slowly added to a cooled chloroform solution of diphenylmethane, a monosulfonic acid was formed; from the chloroform solution diphenylmethane-*o*-sulfone was obtained (299).

(*6*) *Action with alcohols.* If methyl alcohol be allowed to drop slowly into chlorosulfonic acid surrounded by ice, an energetic action takes place. If the acid is added to the alcohol, the same reaction takes place but a portion of the hydrogen chloride reacts with the alcohol, producing the chloride and water. If the temperature be allowed to rise during the action, a considerable amount of ethyl chlorosulfonate is produced, $ClSO_2OC_2H_5$. This is an oily liquid which does not solidify at −30°C.; it is soluble in absolute ether (55).

Levaillant and Simon (185) found that in the Claesson–Ullman process the following reactions take place:

$$ClSO_2OH + CH_3OH \rightarrow HCl + CH_3OSO_2OH \text{ (below } -5°\text{C.)}$$

$$2CH_3OSO_2OH \rightarrow (CH_3)_2SO_4 + H_2SO_4 \text{ (below 130–140°C. } \textit{in vacuo}\text{).}$$

If, however, chlorosulfonic acid and methyl chlorosulfonate are heated to 90–100°C. for several hours and the product is fractionated *in vacuo*, methyl chlorosulfonate begins to boil at 40°C. at 16 mm., most of it passing over at 50–55°C. together with a little chlorosulfonic acid; if the bath is next heated to 190–200°C., unchanged chlorosulfonic acid passes over, accompanied by a little methyl chlorosulfonate and some methyl sulfate, while the residue is mainly sulfuric acid. When various proportions were used, the yield of methyl chlorosulfonate varied from 0.4 to 0.6 mole. The reaction

$$ClSO_2OCH_3 + CH_3OSO_2OH \rightarrow ClSO_3H + (CH_3)_2SO_4$$

is also believed to take place. The crude methyl chlorosulfonate is a colorless liquid, boiling at 42°C. at 16 mm. and at 134–135°C. at 760 mm. with some decomposition. Its density is 1.514 at 0°C. and 1.492 at 15°C.; $n_D^{17°}$, 1.414. It solidifies in a mixture of carbon dioxide and acetone, and melts at about -70°C. It is strongly lachrymatory. It does not mix with sulfuric acid, but is miscible with its chlorine and methyl derivatives, as well as with many organic solvents (185).

In the action of chlorosulfonic acid upon ethyl alcohol, ethyl sulfate is formed. It is a faint yellow inodorous liquid which dissolves in water in all proportions with formation of ethylsulfuric acid, but in alcohol without undergoing any change; it is miscible with ether and benzene, but is reprecipitated by excess (241). McIntosh (199) found that at low temperatures, $-50°$ to -80°C., chlorosulfonic acid forms ethyl hydrogen sulfate and hydrogen chloride in reacting with ethyl alcohol.

Walter (351) found that when glycerol is heated with chlorosulfonic acid at 100–170°C. there results a glyptal resin.

(7) *Action with phenols.* Chlorosulfonic acid is added to phenol in carbon disulfide, and the mixture is cooled to -15°C. and stirred; after 2.5 hr. the carbon disulfide is decanted, and by proper treatment there is separated phenylsulfuric acid, $C_6H_5SO_4H$, and *p*-phenolsulfonic acid, *p*-$HOC_6H_3SO_3H$ (48). Equivalent quantities of phenol and chlorosulfonic acid give phenol-2,4-disulfonyl chloride, m.p. 89°C.; after heating the above substances at 130–140°C. for 4 to 5 hr. the product is phenol-2,4,6-trisulfonyl chloride, m.p. 193°C. (256). Orlowsky (241) prepared phenyl sulfate by the action of phenol on chlorosulfonic acid; it is a thick, oily, more or less dark-colored liquid which decomposes at once in water.

Burkhardt (48) obtained *p*-tolylsulfuric acid, $CH_3C_6H_4SO_4H$, by adding chlorosulfonic acid to a carbon disulfide solution of *p*-cresol. Pollak, Gebauer-Fuelnegg, and Riesz (256) obtained 2-hydroxytoluene-3,5-disulfonyl chloride (*o*-cresol-4,6-disulfonyl chloride), m.p. 85–86°C., when *o*-cresol and chlorosulfonic acid, either in equivalent amounts or with excess acid, were allowed to react at room temperature. *m*-Cresol gives *m*-cresol-4,6-disulfonyl chloride, m.p. 84–89°C. If the equivalent amount of chlorosulfonic acid is added to *m*-cresol there is formed principally *m*-cresolsulfonic acid, but also di-*m*-cresyl sulfate, m.p. 119°C. Heating *o*-cresol with chlorosulfonic acid (10 parts) at 110°C. gives *o*-methylphenylene-*o*-sulfonylide-*p*,*p*′-disulfonyl chloride, which decomposes at 280°C., and is stable in boiling water or alcohol. *m*-Cresol and 10 parts of chlorosulfonic acid, heated at 110°C. for 1.25 hr., give *m*-cresolsulfonylide disulfonyl chloride, which decomposes at 290°C.; heating for 6 hr. at 130–140°C. and pouring into concentrated hydrochloric acid gives *m*-cresol-2,4,6-trisulfonyl chloride, m.p. 151°C. *p*-Cresol likewise gives *p*-cresolsulfonylide disulfonyl chloride, which decomposes at 280°C. Haworth and Lapworth (136), by treating chlorosulfonic acid with a carbon disulfide solution of *m*-cresol at -15°C., formed *m*-tolyl hydrogen sulfate along with *m*-cresol-6-sulfonic acid. *m*-Cresol-4,6-disulfonic acid was produced by the action of 2 moles of chlorosulfonic acid on a carbon disulfide solution of *m*-cresol.

The action of chlorosulfonic acid on catechol for 24 hr. at ordinary temperature yields the disulfonic acid, 1,2,3,5-$(HO)_2C_6H_2(SO_3H)_2$, but if the reaction mixture is heated at 110°C. for 1.5 hr., catechol-3,5-disulfonyl chloride, m.p. 149–150°C., is obtained. Heated at 150°C. for 8 hr. the reaction mixture yields the neutral sulfate of catechol-3,5-disulfonyl chloride, $(SO_2Cl)_2C_6H_2SO_2$, m.p. 143°C. (253).

Quinol, treated with 10 parts of chlorosulfonic acid at the ordinary temperature, yields no products which are insoluble in water or hydrochloric acid. Heated with chlorosulfonic acid at 150–160°C. for 8 hr. it yields chloranil, together with by-products which are best obtained by using 50 parts of chlorosulfonic acid and heating for 80 hr.; these products are pentachlorophenol, m.p. 189°C., and *p*-dichlorobenzodiquinoyl (253).

Resorcinol and chlorosulfonic acid in carbon disulfide at 0°C. or at room temperature (using up to five times the theoretical quantity of chlorosulfonic acid) give 1,3-dihydroxybenzene-4,6-disulfonic acid. Ten parts of chlorosulfonic acid with resorcinol at room temperature gives resorcinol-4,6-disulfonyl chloride, m.p. 178–179°C. Resorcinol and 50 parts of chlorosulfonic acid, heated for 2 hr. at 110°C., give resorcinol-2,4,6-trisulfonyl chloride, m.p. 168°C.; resorcinol and 100 parts of chlorosulfonic acid, heated 110 hr. at 160–170°C., give hexachlorobenzene (252).

Chlorosulfonic acid acts on α-naphthol at ordinary temperature, the 2-sulfonic acid derivative crystallizing out. With an excess of chlorosulfonic acid (five times the weight of α-naphthol for 2.5 hr., or ten times the weight for 1.5 hr.) there results 1-naphthol-2,4-disulfonyl chloride, m.p. 149°C. Prolonged action (4 to 5 days) gives 1-naphthol-2,4,7(?)-trisulfonyl chloride, m.p. 172°C. At 100°C. chlorosulfonic acid and α-naphthol give the 4-sulfonic acid derivative; at 160°C., a black product, or with an excess of chlorosulfonic acid, a resinous product, is obtained, from which a trichloronaphthalenesulfonyl chloride, m.p. 214°C., is isolated.

The action of chlorosulfonic acid upon β-naphthol at the ordinary temperature gives only the 1-sulfonic acid derivative; on standing, a mixture of disulfonyl chlorides is obtained. Excess of chlorosulfonic acid yields a mixture of two disulfonyl chlorides, m.p. 111°C. and 177°C. Heating chlorosulfonic acid and β-naphthol at 130–140°C. gives 2-naphthol-3,6,8-trisulfonyl chloride, m.p. 196°C. Heating β-naphthol with 50 parts of chlorosulfonic acid for 80 hr. at 150–160°C. gives a compound containing chlorine but not sulfur, m.p. 120–122°C. (a dichloronaphthalene (?)) and a sulfur-containing compound, m.p. 136–140°C., probably a naphthoquinone derivative (255).

Phloroglucinol, treated with ten times its weight of chlorosulfonic acid at ordinary temperature, yielded the trisulfonic acid, which, however, could not be freed from inorganic acids and was isolated as the ammonium salt. At higher temperatures or with twenty to fifty times the quantity of chlorosulfonic acid, phloroglucinol yielded phloroglucinol-2,6-disulfonyl chloride, m.p. 184°C. The potassium salt of the disulfonic acid, treated with 6 moles of chlorosulfonic acid, was converted into the trisulfonic acid. At 150–160°C. the reaction between phloroglucinol and chlorosulfonic acid yielded pentachlorophenol and hexachlorobenzene (254).

The action of chlorosulfonic acid on pyrogallol for 45 min. at 100°C. yields the disulfonyl chloride, m.p. 178°C. (decomposition); at higher temperatures pentachlorophenol and hexachlorobenzene are obtained (254).

Treatment of *o*-xylenol, 2,3-$(CH_3)_2C_6H_3OH$, with 10 parts of chlorosulfonic acid at −5°C. to 0°C. for 24 hr. gives 2,3,2′,3′-tetramethyldiphenyl-1,6,1′,6′-sulfonylide-4,4′-disulfonyl chloride, which decomposes at 295°C., and also 2,3-dimethylphenyl-4,6-disulfonyl chloride, which melts at 104–105°C. *o*-Xylenol with 10 parts of chlorosulfonic acid at −5°C. to 0°C. for 4 hr. gives only water- or hydrochloric acid-soluble products. One part of the alcohol and 10 parts of the acid, heated at 110°C. for 2 hr., give 2,3,2′,3′-tetramethyldiphenyl-1,6,1′,6′-sulfonylide-4,4′-disulfonyl chloride and 4,4′-disulfonanilide, m.p. 273°C. The 3,4-compound with 10 parts of the acid gives 3,4-dimethylphenol-2,5-sulfonyl chloride, m.p. 72°.; the disulfonanilide melts at 160°C.; the free sulfonic acid couples with *p*-$O_2NC_6H_4N_2X$, giving a bright red solution which dyes animal fibers. The 2,5-compound, 2,5-$(CH_3)_2C_6H_3OH$, with 10 parts of chlorosulfonic acid gives 2,5-dimethylphenol-3,6-disulfonyl chloride, m.p. 58°C.; the disulfonanilide melts at 173°C.; the free acid gives an orange-yellow dye with *p*-$O_2NC_6H_4N_2X$. The 3,5-compound, 3,5-$(CH_3)_2C_6H_3OH$, and chlorosulfonic acid give a mixture in varying proportions, depending upon the temperature of the reaction, of the two disulfonyl chlorides, m.p. 89–91°C. and 117–119°C.; the two disulfonanilides melt at 160–161° and 205–207°C. The 2,4-compound, 2,4-$(CH_3)_2C_6H_3OH$, gives 2,4-dimethylphenol-6-sulfonyl chloride, m.p. 93–95°C. and 1,3,1′,3′-tetramethyldiphenyl-4,5,4′,5′-sulfonylide, which decomposes above 300°C. (164).

When a well-cooled chloroform solution of guaiacol is treated with chlorosulfonic acid, there is first formed *o*-methoxyphenyl hydrogen sulfate, but if the mixture be allowed to remain for a few minutes, a white crystalline, deliquescent precipitate of guaiacolsulfonic acid is produced (188).

When thiophenol is allowed to react with chlorosulfonic acid the following reaction takes place (14):

$$2C_6H_5SH + ClSO_2OH \rightarrow (C_6H_5)_2S_2 + SO_2 + H_2O + HCl$$

(*8*) *Action with aldehydes.* Paraformaldehyde (or other formaldehyde-generating compounds) reacts with chlorosulfonic acid below 70°C. to give chloromethyl chlorosulfonate, b.p. 49–50°C. at 14 mm., and methylene sulfonate, m.p. 153°C.; above 70°C. there are obtained chloromethyl sulfate, b.p. 96–97°C. at 14 mm., and dichloromethyl ether, b.p. 101.5–102°C. The chloromethyl chlorosulfonate may be converted by chlorosulfonic acid at 70–80°C. into methylene sulfate. The products are useful as alkylating agents and as insecticides. Fuchs and Katcher (104) obtained German patent 505,687 (October 18, 1928) for this method of preparation.

Distillation of the product resulting from the reaction between chlorosulfonic acid and polymerized formaldehyde gave a mixture of chloromethyl chlorosulfonate and chlorosulfonic acid, boiling at 40–60°C. at 11–14 mm.; when 1.25 mole of chlorosulfonic acid per mole of formaldehyde was used there was obtained, together with the above distillate, a small amount of a higher boiling oil, and the residue in the flask solidified after a time to a cake which proved to be methylene sulfate. With 2.5 moles of chlorosulfonic acid an amount of the formaldehyde corresponding to the methylene sulfate was converted into chloromethyl chlorosulfonate. If, in the reaction between 1.25 moles of chlorosulfonic acid and 1 mole of formaldehyde, the temperature is not allowed to rise above 70–80°C., there is obtained, on pouring upon ice, a heavy oil which, when dried and distilled up to 120°C. under atmospheric pressure, gives hydrogen chloride, polymerized formaldehyde, and a small amount of dichloromethyl ether; distillation of the residue in *vacuo* gives, together with a further small amount of formaldehyde, chiefly dichlorodimethyl sulfate, $(ClCH_2O)_2SO_2$; the separation of polymeric formaldehyde is always accompanied by liberation of hydrogen chloride and is to be ascribed to the hypothetical chloromethyl alcohol presumably formed in the reaction. To avoid pouring the reaction product upon ice to destroy the excess chlorosulfonic acid and sulfuric acid, sodium chloride and anhydrous potassium sulfate were used to separate the oil. If the reaction between formaldehyde and chlorosulfonic acid is carried out in the cold and an equivalent amount of sodium chloride is added an almost acid-free oil can be obtained by simple decantation, and distillation gives a materially higher yield of dichlorodimethyl ether. With potassium sulfate instead of sodium chloride, distillation gives, along with dichlorodimethyl ether and dichlorodimethyl sulfate, chiefly chloromethyl chlorosulfonate. Since vacuum distillation of the products of the reaction of chlorosulfonic acid and formaldehyde gives chloromethyl chlorosulfonate (and methylene sulfate) as the sole water-insoluble substances, it seems likely that dichlorodimethyl sulfate on vacuum distillation with chlorosulfonic acid changes into these compounds; as a matter of fact, from pure dichlorodimethyl sulfate and chlorosulfonic acid was obtained, depending upon the relative amounts of the two substances used, either a mixture of chloromethyl chlorosulfonate and methylene sulfate, or chloromethyl chlorosulfonate alone. Dichlorodimethyl ether reacts with chlorosulfonic acid at 60–70°C. and on distillation yields chloromethyl chlorosulfonate exclusively, but if the product is poured upon ice, there separates a mixture of chloromethyl chlorosulfonate and dichlorodimethyl sulfate (102).

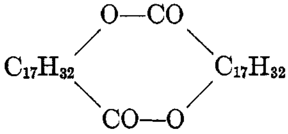
Acetaldehyde and paraldehyde react vigorously with chlorosulfonic acid, yielding dark products which are soluble in water and are not analogous to those derived from formaldehyde. When chloral is treated at room temperature with chlorosulfonic acid, octachlorodiethyl ether, $(CCl_3CHCl)_2O$, b.p. 130–131°C. at 11 mm., m.p. 47°C., which separates when the reaction mixture is cooled to -50°C., is produced; hydrogen chloride and carbonyl chloride are evolved. Metachloral and chloral hydrate give similar results (103).

(*9*) *Action with acids.* Chlorosulfonic acid reacts with oleic acid to split off hydrogen chloride and form sulfoöleic acid (258).

Upon treating chlorosulfonic acid with undecylenoic acid there is formed hydroxysulfoundecanoic acid, free from chlorine. Its analysis by Bauer (8) proves that all sulfo fatty acids, whether produced by chlorosulfonic acid or sulfuric acid, add OH and SO_3H at the double bond of the acid and differ from each other only in the amount added. Pomeranz (259) suggests that a sulfonation of undecylenoic acid by means of sulfur trioxide would definitely decide how the sulfonic acid group adds to unsaturated aliphatic acids.

The action of chlorosulfonic acid on $\Delta^{9,10}$-undecenoic acid in ether gives an oil which loses chlorine when its ether solution is shaken with sodium sulfate, giving 10-hydroxy-11-sulfo- and 11-hydroxy-10-sulfo derivatives of undecenoic acid; these two products (which have not been studied structurally) melt at 208–209°C. and 186–187°C. (8).

If ricinoleic acid and chlorosulfonic acid are allowed to react in aqueous solution for some time, or if the solution is heated, no compound is formed, but rather there results sulfuric acid and $C_{17}H_{32}CO\cdot O\cdot C_{17}H_{32}COOH$, a yellow viscous oil. On further heating there is formed a lactide of ricinoleic acid (121):



Thioindigoid dyes, probably thioindigotindithioglycolic acids, are obtained when benzene-1,2-dithioglycolic acid, benzene-1,3-dithioglycolic acid, benzene-1,4-dithioglycolic acid, 4-chlorobenzene-1,3-dithioglycolic acid, and 2,5-dichlorobenzene-1,3-dithioglycolic acid are treated with chlorosulfonic acid at 50–60°C. These dye wool and cotton with red to violet shades; they are usually better when used in an acid bath (110).

Upon condensing 1,4-benzoquinone-2,5(2,6?)-dithioglycolic acid with an excess of chlorosulfonic acid at 50–70°C. for 12 hr. there is formed a thioindigoid dye, an intensely violet substance which dyes cotton as well as wool a greenish blue color (109).

Salicylic acid, when treated with 10 parts of chlorosulfonic acid at 130–140°C. for 1.5 hr., yields the disulfonyl chloride, m.p. 185°C. (253).

One part of 1-naphthol-2,4-disulfonic acid, allowed to stand with 10 parts of chlorosulfonic acid at room temperature for 3 days, produced crystals which proved to be 1-naphthol-2,4,7-trisulfonyl chloride, m.p. 174°C. This same product was obtained after 3 hr. when the reaction mixture was cautiously poured onto crushed ice.

One part of the sodium salt of 1-naphthol-4,7-disulfonic acid was slowly added to 10 parts of chlorosulfonic acid; after standing for 14 days the crystals were isolated and found to be the same as above, 1-naphthol-2,4,7-trisulfonyl chloride. This compound is also obtained after a 3-hr. reaction period from 1-naphthol-4,7-disulfonic acid and chlorosulfonic acid at room temperature.

1-Naphthol-4,8-disulfonic acid, added to 10 parts of chlorosulfonic acid and heated in an oil bath for 1 hr. at 150°C., forms 1-naphthol-4,6,8-trisulfonyl chloride, m.p. 217°C.

If 1-naphthol-4,6-disulfonic acid is treated analogously at 100–150°C., and the reaction product is poured into concentrated hydrochloric acid and recrystallized from carbon disulfide, crystals are obtained which melt at 217°C. and are identical with those obtained above (108).

Chlorosulfonic acid and hydrogen sulfide react at ordinary temperatures forming sulfuric acid, hydrogen chloride, sulfuryl chloride, and sulfur (264).

(10) Action with acid chlorides. The reaction products of chlorosulfonic acid with the first three aliphatic acid chlorides, formed at various temperatures, were investigated by Krajčinovič (176). In the case of acetyl chloride the temperatures 20°, 45°, 60°, 100°, and 140°C. were used. One of the two sulfonic acids isolated on hydrolysis with water was found to be $CH_2(SO_3H)COOH$:

$$CH_3COCl + ClSO_3H \rightarrow CH_3COSO_3Cl + HCl$$

$$CH_3COSO_3Cl \xrightarrow[\text{rearrangement}]{\text{intramolecular}} CH_2(SO_3H)COCl$$

$$\xrightarrow{+H_2O} CH_2(SO_3H)COOH + HCl$$

At temperatures above 60°C. $CH_2(SO_3H)COOH$ goes over to $CH_2(SO_2H)_2$.

Above 45°C. CH_3COSO_3Cl is transformed into sulfacetyl chloride, which with more chlorosulfonic acid at temperatures above 60°C. is converted into sulfomethanesulfonyl chloride, carbon dioxide, and hydrogen chloride. The substance, $\underline{OC(CH_3)=CHCOCH=C}CH_2COOH$, m.p. 99°C., obtained at temperatures above 60°C., is identified as 2-methylpyrone-6-acetic acid (173).

From equal quantities of propionyl chloride and chlorosulfonic acid, allowed to stand for 5 to 10 days at room temperature and then poured into cold water, is obtained a pitch-like mass from which ether extracts α'-ethyl-β,β'-dimethylpyronone, $C_2H_5\underline{C=C(CH_3)COCH(CH_3)COO}$, m.p. 151°C.; the residue remaining from the ether extract yields $CH_3CH(SO_3H)COOH$. The formation of α'-ethyl-β,β'-dimethylpyronone is explained as follows: The chlorosulfonic acid combines with the propionyl chloride to form $C_2H_5COOSO_2CH(CH_3)COOSO_2CH(CH_3)COCl$; the SO_3 groups are then split off and the resulting $C_2H_5COCH(CH_3)COCH(CH_3)COCl$ partly enolizes at the δ-carbon atom, and the ring in α'-ethyl-β,β'-dimethylpyronone is closed by elimination of hydrogen chloride (174).

The action of chlorosulfonic acid on butyryl chloride at room temperature is gradual and is accompanied by a continuous evolution of hydrogen chloride and carbon monoxide. No $C_2H_5CH(SO_3H)COOH$ could be obtained; extraction with ether yielded dipropyl ketone, b.p. 144°C.

The results with the three chlorides indicate that the greater the number of carbon atoms in the chloride, the fewer the number of moles that condense. Thus, 4 moles of acetyl chloride condense to form 2-methyl-1,4-pyrone-6-acetic acid, 3 moles of propionyl chloride to form α'-ethyl-β,β'-dimethylpyronone, and only 2 moles of butyryl chloride to form dipropyl ketone. The condensation products of acetyl chloride are obtained only at higher temperatures, whereas those of the other chlorides are decomposed at the higher temperatures and can be isolated only at room temperature (175). In the reaction of propionyl and butyryl chlorides with chlorosulfonic acid at ordinary temperatures carbonyl chloride groups are split off to some extent, as is shown by the continuous evolution of carbon monoxide (176).

(11) Action with aryl halides. When chlorobenzene and 3 parts of chlorosulfonic acid are heated for 8 hr. at 150–180°C. there is formed $2,4\text{-}(ClO_2S)_2C_6H_3Cl$, m.p. 90–91°C. (257). Equimolar quantities of the halide and acid produce chlorobenzenesulfonic acid and a dichlorosulfobenzide, $(C_6H_4Cl)_2SO_2$ (14).

A dibromosulfobenzide was formed when 1 mole of the halide reacted with chlorosulfonic acid; it crystallized from alcohol in long needles, melting at 172°C., and boiling without decomposition at a higher temperature. A bromobenzenesulfonic acid was also obtained (14). Under similar conditions Armstrong (5) obtained the dibromosulfobenzide, $(C_6H_5Br)_2SO_2$, which is soluble in hot alcohol, but difficultly soluble in cold alcohol; it melts at 168°C.

(12) Action with sulfones. Ten parts of chlorosulfonic acid heated at 150–160°C. with di-*p*-xylyl sulfone gives di(*p*-xylylsulfonyl chloride) sulfone, m.p. 190°C. (257).

Ethyl sulfone and chlorosulfonic acid heated for 6 hr. at 150–160°C. give ethyl-*m*-chlorosulfonylphenyl sulfone, m.p. 93.5°C. (257).

(13) Action with substituted amides of cyanoacetic acid. The following compounds were prepared by treating a substituted amide of cyanoacetic acid with an excess of chlorosulfonic acid in dry chloroform: disulfocyanoacetanilide, $(HO_3S)_2C(CN)CONHC_6H_5$, leaflets; the corresponding *o*-, *m*-, and *p*-toluides; the α-naphthylamide; the β-naphthylamide, yellow needles; the benzylamide, colorless plates; the xylide (1,4,5-), colorless shining scales. These compounds are very soluble in water and almost insoluble in alcohol, chloroform, carbon disulfide, carbon tetrachloride, benzene, toluene, ether, and petroleum ether. They char when heated to 255–280°C. The reactivity of the methylene hydrogen with chlorosulfonic acid, which is absent with cyanoacetic acid, increases as phenyl, tolyl, and naphthyl radicals are substituted in the amide group, showing that the rapidity with which the reaction proceeds depends on the electronegative character of the group (228).

(14) Action with miscellaneous reagents. Aniline in excess of chlorosulfonic acid, heated to 150–160°C. for 2 hr. with sodium chloride, slowly reacts to give, on adding water, aniline-2,4,6-trisulfonyl chloride, m.p. 175°C. The acid chloride is obtained in only small yield if sodium chloride is absent (the free acid then being formed). *p*-Toluidine gives a 3,5-disulfonyl chloride, yellow needles, m.p. 156°C.; *m*-phenylenediamine gives the 4,6-disulfonyl chloride, m.p. 274–275°C.; *p*-phenylenediamine gives the tetrachloro derivative (189).

Benzenesulfonyl chloride, heated with 3 parts of chlorosulfonic acid for 8 hr. at 150–180°C., gives $2,4\text{-}(ClO_2S)_2C_6H_3Cl$, m.p. 90–91°C. (257).

p-Chloronitrobenzene and chlorosulfonic acid, heated for 6 to 7 hr. at 160–170°C., give $4,2\text{-}O_2N(ClO_2S)C_6H_3Cl$, m.p. 89°C. (257).

Nitrobenzene and chlorosulfonic acid heated for 20 hr. at 150°C. give chloranil (257).

Thiophenetole and chlorosulfonic acid heated at 150–160°C. give pentachlorophenylethyl sulfide (257).

α- and β-naphthylaminesulfonates are sulfonated by chlorosulfonic acid. With the α-compound the main products are the 4- and 5-sulfonic acids, whereas the β-compound gives the 5- and 8-sulfonic acids (64).

Two moles of toluene sulfhydrate to 1 mole of chlorosulfonic acid forms *p*-toluene disulfide, m.p. 43°C., together with sulfur dioxide and hydrogen chloride (14).

Methyl chlorocarbonate, when poured gradually into chlorosulfonic acid, forms methyl chlorosulfonate, b.p. 31°C. at 12 mm. (172).

Phenyldichloroarsine reacts with chlorosulfonic acid forming benzenesulfonyl chloride (32).

Dewar and Cranston (52) observed that chlorosulfonic acid reacts with carbon disulfide in a sealed tube at 100°C. as follows:

$$CS_2 + ClSO_3H \rightarrow HCl + SO_2 + COS + S$$

In a sealed tube at 120°C. chloroform reacts with the acid as follows:

$$CHCl_3 + ClSO_3H \rightarrow COCl_2 + SO_2 + 2HCl$$

p-Tolyl acetate and 5 parts of chlorosulfonic acid were allowed to stand for 6 days at 15°C.; the only definite product isolated was *p*-cresoldisulfonyl chloride, pale yellow plates, m.p. 105°C. (115).

Aceto-*p*-toluidine in 5 moles of chlorosulfonic acid at 80°C. for 1 hr. gives aceto-*p*-toluidine-2-sulfonyl chloride, colorless prisms, m.p. 124–125°C. (158).

Phenacetin was gradually added to chlorosulfonic acid, the temperature being maintained at 50°C. for 1 hr.; 4-acetylaminophenetole-2-sulfonyl chloride, colorless prisms, m.p. 133°C., was obtained (158).

Aceto-*p*-xylidide when kept in chlorosulfonic acid for 1 hr. at 80°C. formed aceto-*p*-xylidine-6-sulfonyl chloride, colorless needles, m.p. 160°C. (158).

1,3-Dichloro-2-propanol, reacting with chlorosulfonic acid, yields β,β-dichloropropyl hydrogen sulfate, $SO_2(OH)OCH(CH_2Cl)_2$ (32).

Identification

Chlorosulfonic acid in the presence of powdered tellurium gives a cherry-red color; with powdered selenium a moss-green color (293).

III. TITANIUM TETRACHLORIDE, $TiCl_4$

Preparation

George (111) prepared titanium tetrachloride in 1825 by passing dry chlorine over heated titanium; Vigouroux and Arrivaut (344) and de Carli (72) passed chlorine over ferro-titanium heated to red heat; Friedel and Guérin (98) prepared it by heating crystals of titanous oxychloride; Ellis (88) ignited a mixture of rutile and powdered aluminum and heated the product in a current of chlorine; Hunter (148), Goerges and Stähler (119), and Oreshkin (240) heated titanium carbide in a stream of chlorine;

Friedel and Guérin (98) and Pamfilov and Shtandel (246) passed chlorine over heated titanium dioxide; Dumas (84) passed chlorine over a red-hot mixture of titanium dioxide and carbon. Pierre (251), Demoly (76), von der Pfordten (345), Merz (204), Oreshkin (240), and Wagner (347) also used the chlorine–carbon process, as did McInerny, Williams, and Glaze (198), who obtained U. S. patent 1,888,996 (November 29, 1932) for the process. Watts and Bell (353) passed carbon tetrachloride, chloroform, or a mixture of chlorine and carbon monoxide over red-hot titanium dioxide; Priesz (262) used chloroform as the chlorinating agent with a little carbon mixed with the titanium dioxide. Demarçay (75) found the action of carbon tetrachloride on titanium dioxide very fast at 440°C. and considered this to be one of the most convenient methods of preparation. Bourion (42) prepared the tetrachloride by the action of the vapor of sulfur monochloride and chlorine on red-hot titanium dioxide. Beloglazov (19) made briquets from ground titanium ore mixed with carbon and a binder such as starch paste and then chlorinated the briquets. Favre (93) obtained French patent 800,688 (July 16, 1936) for the preparation of the tetrachloride by chlorinating a mixture of titanium, copper, and iron; Nakrav (229) obtained Hungarian patent 115,530 (December 1, 1936) for its preparation by chlorinating material containing titanium and iron; Société des Produits Chimiques de Saint-Bueil (312) obtained British patent 458,892 (December 29, 1936) for its preparation by chlorinating titanium–iron–copper mixtures above 150°C.; Barton (6) obtained U. S. patent 1,179,394 (April 18, 1915) for the preparation of the tetrachloride by heating a mixture of titanium dioxide and soft coal until the volatilizable constituents were driven off and then treating the remaining cinder with chlorine at a temperature of 650°C.

Physical properties

Titanium tetrachloride is a transparent, colorless, mobile liquid. Its boiling point has been reported as follows: 134.8°C. at 735 mm. (89); 135.0°C. at 760 mm. (85, 130, 167, 273); 135.6–135.8°C. at 758 mm. (142); 136.0°C. at 750 mm. (39); 136.0°C. at 753 mm. (105); 136.0°C. at 760 mm. (88, 119, 344); 136.0°C. at 762.3 mm. (25); 136.4°C. at 760 mm. (334); 136.5°C. at 760 mm. (148). The following values have been given for its melting point: −23°C. (31, 89); −25°C. (132); −30.C. (181).

Titanium tetrachloride has a vapor pressure of 10.05 mm. at 20°C., 16.70 mm. at 30°C., 26.50 mm. at 40°C., 41.15 mm. at 50°C., 62.15 mm. at 60°C., 92.05 mm. at 70°C., 134.00 mm. at 80°C., 190.65 mm. at 90°C., 264.55 mm. at 100°C., 367.15 mm. at 110°C., 493.80 mm. at 120°C., 652.30 mm. at 130°C., and 740.75 mm. at 135°C. (4). Its critical temperature was estimated by Guldberg (127) as 358°C. Its vapor density is

6.836 (air = 1) or 197.4 (oxygen = 16), while the theoretical value is 190 (oxygen = 16) (84). The specific heat of the liquid between 13°C. and 99°C. is 0.18812; the specific heat of the vapor at constant pressure between 163°C. and 271°C. is 0.12897 (271). Regnault (271) determined the heat of fusion at 25°C. as 11.77 cal. per gram; Nasu (231) calculated it from freezing point data of dilute solutions as 12.90 cal. per gram. Its heat of solution is given as 59.03 Cal. (38) or 57.866 Cal. (331). Its heat of neutralization ($TiCl_4$ aq., 4NaOH aq.) is 47.664 Cal. (331). Its heat of formation (TiO_2 aq., 4HCl aq.) is 7.296 Cal. (331). The molecular heat of vaporization of titanium tetrachloride, calculated by the Clausius-Clapeyron equation, is 8960 Cal. for 25°C. and 8620 Cal. at the boiling point (4). The critical solution temperature of $TiCl_4$–SO_2 was found to be 11.9°C. (39). Biltz and Meinecke (31) gave for the freezing point of the mixture of chlorine and titanium tetrachloride the value −22.5°C.; the eutectic is at −108°C. and at a chlorine concentration of 87.5 per cent. Hildebrand and Carter (142) determined the compressibility at 25°C. to be 898 reciprocal atm. and the thermal pressure coefficient (atm. $\times$ liters^2 per mole of liquid) to be 41.90. Bergmann and Engel (22) determined from the dipole moment ($TiCl_4 = 0$) and from the spatial structure that titanium tetrachloride is a regular tetrahedron.

The specific gravity of titanium tetrachloride is as follows: 1.5222 at its boiling point (334), 1.744 at 10.5°C. (118), 1.76041 at 0°/4° (334), 1.76098 at 0°/4°, 1.761 at 18°C. (325), and 1.76139 at 0°C. (292). Values of its density have been reported as follows: $d_{4°}^{15.5°}$, 1.742; $d_{4°}^{26°}$, 1.725; $d_{4°}^{40°}$, 1.701; $d_{4°}^{58.5°}$, 1.673 (105). Its parachor is 262.5 (105). Its viscosity coefficient is 0.007921 at 20°C. and 0.007458 at 25°C. expressed in C.G.S. units (292). Its entropy is 59.51 at 25°C. (271). The values of its index of refraction are as follows: $n_A = 1.5651$; $n_D = 1.6039$; $n_F = 1.6296$; $n_H = 1.6814$ (118). Its molecular refraction is 65.20 (118). Its molecular dispersion is 10.74 (118). Its dielectric constant is 2.73 at 24°C. (196).

Ingersoll (152) found the magnetic rotation of titanium tetrachloride in a concentrated solution of ferric chloride to be nearly proportional to $\lambda/3$; in a solution of potassium ferrocyanide it is almost proportional to $\lambda/5$. Arii (4) found Trouton's constant to be 21.07, which shows that the tetrachloride is a normal liquid. Sulfur dioxide forms with titanium tetrachloride mixtures which are but partly miscible at low temperatures (39). Vaidyanathan (341) showed that titanium tetrachloride has a tetrahedral symmetry and gave the specific susceptibility at 35°C. the value of -0.287×10^{-6}.

Chemical properties

(*1*) *Action with water.* von Kowalewsky (171) showed that titanium tetrachloride dissolves in water with the evolution of much heat, and that the hydrogen chloride liberated during the hydrolysis suffices to redissolve the precipitated hydroxide first formed without any corresponding change in the electrical conductivity. The value of the electrical conductivity shows that equilibrium is established before the hydrolysis is complete; the hydrolysis is completed by boiling, or by heating in a sealed tube at 150°C. König and von der Pfordten (169) found that with water titanium tetrachloride forms a series of oxychlorides: $TiCl_3OH$, $TiCl_2(OH)_2$, $TiCl_2(OH)_3$; with excess of water it forms $Ti(OH)_4$. Wagner (347) found that when titanium tetrachloride is dropped into water, a turbid liquid is produced, but that a clear solution of orthotitanic acid in the tetrachloride can be obtained by adding water drop by drop to the tetrachloride with constant agitation. The tetrachloride emits dense white fumes in air but, according to Pierre (251), although this occurs at ordinary temperature the fuming does not occur below 0°C. The possible use of the fumes for production of clouds in modern warfare has been discussed by Richter (275) and Walker (349).

(*2*) *Action with metals.* Parravano and Mazzetti (248) found that at 900°C. titanium tetrachloride is reduced by iron, forming a titanide; at about 110°C. the tetrachloride is reduced by potassium to the dichloride and partly to titanium (346). Stähler and Bachran (314) showed that the tetrachloride is reduced to the trichloride by heating it with finely powdered aluminum, antimony, arsenic, or tin in a sealed tube at 400°C. Sodium amalgam reduces the tetrachloride to the dichloride (289), and at slightly elevated temperatures aluminum, magnesium, zinc, mercury, arsenic, and tin reduce it to the trichloride (289).

(*3*) *Action with hydrogen.* Titanium tetrachloride is reduced by hydrogen above 600°C., forming the tri- and di-chlorides (300); at red heat Goerges and Stähler (119) found that some titanium was produced. Friedel and Guérin (98) produced titanous oxychloride by passing a mixture of hydrogen and the vapor of titanium tetrachloride over white-hot titanium dioxide.

(*4*) *Action with ammonia and phosphine.* Rose (279) found that dry ammonia is rapidly absorbed by titanium tetrachloride with great evolution of heat; the analysis of the brownish-red product corresponds with titanium tetraamminotetrachloride, $TiCl_4 \cdot 4NH_3$; Persoz (249) obtained a pale yellow powder by Rose's process and the analysis corresponded with titanium hexamminotetrachloride, $TiCl_4 \cdot 6NH_3$; Stähler and Wirthwein (315) also obtained this compound as a saffron-yellow powder by passing the vapor of titanium tetrachloride in a stream of dried hydrogen into ammonia; Rosenheim and Schutte (280) obtained the hexammine as a dark yellow powder by passing dry ammonia into a dry ethereal solution of titanium tetrachloride cooled with ice. According to Stähler and Wirthwein (315), titanium octamminotetrachloride, $TiCl_4 \cdot 8NH_3$, is obtained as a pale yellow powder when titanium tetrachloride is shaken with liquid ammonia for 12 hr.

Rose (279) showed that titanium tetrachloride absorbs phosphine, forming a brown solid, titanium phosphinotetrachloride, which, when heated in a closed vessel, forms hydrogen chloride, phosphine, and a lemon-yellow sublimate of phosphonium chlorotitanate, $3TiCl_4 \cdot 2PH_4Cl$. Höltje (146) produced $TiCl_4 \cdot PH_3$ and $TiCl_4 \cdot 2PH_3$ by the action of phosphine on titanium tetrachloride; both are yellow in color.

(5) Action with hydrogen sulfide. Ebelmen (86) has reported that, in the cold, hydrogen sulfide reduces titanium tetrachloride to the dichloride; at a higher temperature titanium disulfide is formed. Biltz and Keunecke (30) found that dry liquid hydrogen sulfide does not react with or dissolve titanium tetrachloride, but at a higher temperature there is formed a monosulfohydrate, $TiCl_4 \cdot H_2S$, and a disulfohydrate, $TiCl_4 \cdot 2H_2S$, with the respective heats of formation 8.86 Cal. and 8.18 Cal.

(6) Action with cyanides. Wöhler (366) and Schneider (302) obtained the addition products $TiCl_4 \cdot 2HCN$ and $TiCl_4 \cdot CNCl$. Oberhauser (234) obtained the compound $3TiCl_4 \cdot 2BrCN$ from the tetrachloride and cyanogen bromide. Karantassis (162) prepared the addition product $TiCl_4 \cdot 2HCN$ by adding hydrogen cyanide to titanium tetrachloride in a U-tube cooled with ice and salt.

(7) Action with oxygen and nitrogen. A white solid of the composition $Ti_2O_3Cl_2$ was obtained by passing a mixture of oxygen and the vapor of titanium tetrachloride through a red-hot porcelain tube packed with porcelain pieces (339). When titanium tetrachloride is vaporized in a current of nitrogen and passed through the silent electric discharge at 4500 volts there is produced a compound having the formula $TiNC \cdot TiCl_4$ (143).

(8) Action with hydrogen halides. Ruff and Ipsen (288) obtained a citron-yellow titanium fluochloride, approximately $TiClF_3$, by the action of the tetrachloride on hydrogen or silver fluoride. Hautefeuille (135) found that boiling titanium tetrachloride reacts with hydrogen iodide, forming titanium tetraiodide.

(9) Action with phosphorus chlorides. Bertrand (25) observed that phosphorus trichloride unites directly with titanium tetrachloride, forming yellow crystals of titanium phosphorus heptachloride, $TiCl_4 \cdot PCl_3$; Weber (355) obtained titanium phosphoric chloride, $TiCl_4 \cdot PCl_5$, by saturating a mixture of phosphorus trichloride and titanium tetrachloride with dry chlorine, and Wehrlin and Giraud (356) obtained it by heating equimolar proportions of the constituents in a sealed tube to 150°C. Weber (355) prepared titanium phosphoryl heptachloride, $TiCl_4 \cdot POCl_3$, by dropping phosphoryl chloride into titanium tetrachloride.

(10) Action with ether and alcohol. The compound $TiCl_4 \cdot (C_2H_5)_2O$

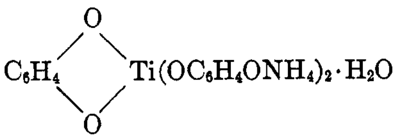
was obtained from the constituents (15, 25, 76, 88, 345). Demarçay (75) found that alcohol reacts with titanium tetrachloride giving crystals of $Ti(OC_2H_5)_3Cl \cdot HCl$, and that this reacts with sodium ethylate, forming ethyl orthotitanate, $Ti(OC_2H_5)_4$. Benrath (20) found that titanium tetrachloride in the presence of alcohol is slowly reduced on exposure to light; Benrath and Obladen (21) found that the photochemical reaction is accompanied by autoöxidation and formation of hydrogen peroxide.

(*11*) *Action with acids.* Demoly (76) evaporated a strongly acid solution of titanium tetrachloride and obtained very hygroscopic crystals of the pentahydrate, $TiCl_4 \cdot 5H_2O$; *in vacuo*, over concentrated sulfuric acid, the dihydrated compound $TiCl_4 \cdot 2H_2O$, results. Benrath (20) showed that titanium tetrachloride in the presence of oxalic, mandelic, or lactic acids is slowly reduced in light. König and von der Pfordten (169) obtained, by regulating the mixing of concentrated hydrochloric acid with titanium tetrachloride, the three intermediate stages of hydrolysis of the tetrachloride: the first stage represented by titanium hydroxytrichloride, $Ti(OH)Cl_3$, the second by titanium dihydroxydichloride, $Ti(OH)_2Cl_2$, the third or penultimate stage represented by titanium trihydroxychloride, $Ti(OH)_3Cl$. Weber (355) passed the dried vapors from aqua regia over titanium tetrachloride and obtained titanium dinitrosyl hexachloride, $TiCl_4 \cdot 2NOCl$. Hampe (183) obtained the same product by the action of hyponitrous acid on the tetrachloride. Clausnizer (59) obtained titanium sulfatotetrachloride, $TiCl_4 \cdot SO_3$, by dropping chlorosulfonic acid into titanium tetrachloride. Rosenheim, Schnabel, and Bilecki (281) prepared the compound $TiCl(OC_6H_4COOH)_3 \cdot HCl$ by boiling 3 moles of salicylic acid in absolute ether with titanium tetrachloride; the product formed purple-red crystals, melting at 115°C. (decomposition). Dermer and Fernelius (77) prepared the compound $Cl_2Ti[OC_6H_2(NO_2)_3]_2$ by the reaction of picric acid with titanium tetrachloride.

(*12*) *Action with ketones.* Dilthey (82) made substitution products of titanium tetrachloride with acetylmethylacetone, triacetylmethylacetonyltitanium titanichloride, $[Ti\{OC(CH_3){=}C(CH_3)(CH_3CO)\}_3Cl]_2 \cdot TiCl_4$. Evard (91) and Scagliarini and Tartarni (297) prepared the compound $Ph_2CO \cdot TiCl_4$, a clear yellow, crystalline mass, by precipitating benzophenone in anhydrous benzene with a benzene solution of titanium tetrachloride.

(*13*) *Action with acetyl-β-glucosides.* Tetraacetyl-β-hexylglucoside (m.p. 51.5°C.) in chloroform, when treated with a chloroform solution of titanium tetrachloride and boiled for 75 min. on a water bath, gives the α-isomer (m.p. 61°C.) (242); tetraacetyl-β-cyclohexylglucoside (m.p. 120–121°C.) in chloroform, treated with a chloroform solution of titanium tetrachloride for 75 min., gives the α-isomer (m.p. 40–41°C.) (243); heptaacetyl-β-methylcellobioside in chloroform, heated for 6 hr. with a chloroform solution of titanium tetrachloride, yields the α-isomer (m.p. 185°C.) (244); an absolute chloroform solution of titanium tetrachloride, added to a similar solution of ethyl tetraacetyl-β-d-glucosidoglycolate, refluxed for 2.5 hr., cooled, and poured into ice water, produces acetochloroglucose, m.p. 71.5–72.5°C. (274).

(*14*) *Miscellaneous reactions.* Davis (70) reported that titaniumnitrogensulfotrichloride, $2TiCl_3\cdot N_4S_4$, is formed in orange crystals when titanium tetrachloride is added to a solution of nitrogen sulfide in chloroform. Wölbling (367) obtained titaniumnitrogensulfotetrachloride, $TiCl_4\cdot N_4S_4$, by the interaction of the components dissolved in carbon tetrachloride. Ruff (285) reported the formation of titanium sulfoöctochloride, $TiCl_4\cdot SCl_4$, by dropping acid sulfur chloride into a solution of titanium tetrachloride in sulfuryl chloride. Weber (355) obtained titanium selenium dioxyoctochloride, $TiCl_4\cdot 2SeOCl_2$, by dropping selenium oxydichloride into titanium tetrachloride. Rosenheim and Sorge (282), upon the addition of 3 moles of pyrocatechol to an ether solution of 1 mole of titanium tetrachloride, obtained a deliquescent, non-homogeneous product which, on evaporating off the ether and rendering neutral with ammonia, gave the ammonium salt



$$C_6H_4\begin{smallmatrix}O\\ \\O\end{smallmatrix}Ti(OC_6H_4ONH_4)_2\cdot H_2O$$

Kashtanov (163) prepared trimethylmethane by treating a benzene solution of diphenylethoxymethane with titanium tetrachloride. 5-Chloro-2-furyl ethyl ketone (m.p. 55°C.) was prepared by Gilman, Burtner, Calloway, and Turck (117) by treating 2-nitrofuran and propionyl chloride with titanium tetrachloride. Titanium tetrachloride reacts with phenol as follows:

$$TiCl_4 + C_6H_5OH \rightarrow HCl + TiCl_3OC_6H_5$$

The trichlorotitanium phenolate obtained can be hydrolyzed thus:

$$TiCl_3OC_6H_5 + 5H_2O \rightarrow C_6H_5OH + Ti(OH)_4\cdot H_2O + 3HCl$$

Colorimetric investigations of the trichlorotitanium phenolate solution show that selective light absorption by this solution follows the Lambert–Beer law. The reaction can be used as a basis for colorimetric determination of either titanium tetrachloride or phenol (187). Titanium tetrachloride is a catalyst in the polymerization of cyclopentadiene (316). Addition of titanium tetrachloride in chloroform to chloroform solutions of heliotropin and methyl phthalate precipitates the following crystalline addition compounds: $TiCl_4 \cdot C_6H_4(COOCH_3)_2$, bright yellow, unstable in moist air, and $TiCl_4 \cdot 2\underline{C_6H_3(CHO)OCH_2O}$, bright red, very unstable, fuming in air (297).

IV. SILICON TETRACHLORIDE, $SiCl_4$

Preparation

Silicon tetrachloride was first prepared by Berzelius (26) in 1823 by the direct union of the elements. It was later prepared by Oersted (236), Buff and Wöhler (47), Ebelmen (87), Schnitzler (303), and Baxter, Weatherill, and Holmes (11) by passing chlorine over an intimate mixture of silicon and charcoal at red heat. Brallier (43) prepared it by passing chlorine over a mixture of silicon and silicon carbide; Hempel and von Haasy (137) by treating sulfosilicates with chlorine; Robinson and Smith (277), Warren (352), de Carli (72), and Martin (192) by passing chlorine over heated ferrosilicon; Gattermann (106) used magnesium silicide; Rauter (270) used copper silicide; Hutchins (150) used silicon carbide; Vigouroux (342) used aluminum silicide. Weber (354) prepared it by heating silicochloroform with chlorine. Stock, Somieski, and Wintgen (326) found that disiloxane and chlorine react vigorously at −125°C., forming tetrachloromonosilane.

Deville (78) showed that hydrogen chloride might be employed in place of chlorine but that the temperature would have to be higher; Currie (66) made the same observation. Faure (92) obtained silicon tetrachloride by passing a mixture of hydrogen chloride and a hydrocarbon over red-hot silica. Stock and Zeidler (327) prepared it by treating cupric silicide with hydrogen chloride at 300°C. Montemartin and Losana (222) found that, upon heating mixtures of aluminum and potassium silicates with carbon at high temperatures in a current of nitrogen, a cyanide was formed which, when heated to about 1000°C. in a current of dry gaseous hydrogen chloride, produced silicon tetrachloride.

Weber (354) and Daubrée (68), by strongly heating amorphous silica, powdered quartz, or a powdered silicate in the vapor of phosphorus pentachloride, obtained silicon tetrachloride. Didier (81) prepared silicon tetrachloride by heating cerium trichloride and silica in the presence of a weak oxidizing agent; Matignon and Bourion (194) by passing a mixture of chlorine and the vapor of sulfur chloride over silica at 450°C.; Baudrimont (7) by heating a mixture of potassium chlorate and silica above 360°C.; Friedel and Ladenburg (99), Buff and Wöhler (47), and Stock and Zeidler (327) by decomposing silicochloroform by heat; Stokes (328) by the reaction of the aromatic silicon esters with phosphorus oxychloride;

Colson (61) by reacting mercuric chloride with silicon sulfide; Budnikov and Shilov (45) by the action of sulfur monochloride on silica at 1000°C. and (46) by passing a stream of phosgene over powdered silica at 900–1000°C.

Hutchins (149, 151) obtained Canadian patent 184,354 (May 14, 1918) and U. S. patent 1,271,713 (July 9, 1918) for the preparation of silicon tetrachloride by passing dry chlorine over silicon carbide heated to almost 1000°C., and Moore (224) obtained U. S. patent 1,350,932 (August 24, 1920) for a process differing only in detail. Jüngst and Mews (160) obtained German patent 157,615 for the preparation of silicon tetrachloride by heating metal chlorides with silicon. The consortium fur Electrochemische Industrie-Ges. (62) obtained British patent 176,811 (March 13, 1922) for the preparation of silicon tetrachloride by passing chlorine, containing sulfur monochloride, over a heated mixture of silica and carbon.

Physical properties

Silicon tetrachloride is a transparent, colorless liquid, which fumes at ordinary temperatures. Berzelius (26) stated that the liquid evaporates as a white cloud, leaving a residue of silica. The vapor has a suffocating odor and reddens litmus paper.

The boiling point of silicon tetrachloride has been reported as follows: 50°C. (309); 56.8°C. (326, 365); 56.8°C. at 751 mm. (40); 56.81°C. (272); 56.9°C. (12); 57°C. (165); 57.02–57.05°C. (277); 57.50–57.55°C. at 755 mm. (142); 57.57°C. at 769 mm. (12); 58°C. (11, 131); 58.0–58.5°C. at 765.33 mm. (333); 59°C. at 766 mm. (83, 194, 251). Its melting point has been reported as −68.7°C. (326), −69.7°C. (40), −70°C. (181), −89°C. (12), and −102°C. (270).

The specific gravity of silicon tetrachloride is 1.1929 at 99.9°C. (203), 1.47556 at 22°C. (1), 1.481245 at 20°C. (277), 1.4878 at 20°C. (131), 1.4928 at 15°C. (203), 1.4933 at 15°C. (287), 1.50068 at 10.98°C. (203), 1.522 (97), 1.52371 at 0°C. (251), 1.524 at 16°C. (325), 1.52408 at 4°C. (333), and 1.54 (170). Its vapor density has been reported as 5.939 (83), 5.86 (observed) and 5.868 (calculated) (272). The values found for its surface tension were: 16.31 dynes per centimeter at 18.9°C., 13.66 dynes per centimeter at 45.5°C. (269), and 19.70 dynes per centimeter at 20°C. (219). Its specific cohesion is 2.24 sq. mm. at 18.9°C. and 1.95 sq. mm. at 45.5°C. (269). Its vapor pressure has been reported as follows: 11.6 mm. at 0°C., 13.3 cm. at 5°C., 15.0 cm. at 10°C., 17.5 cm. at 15°C., 21.6 cm. at 20°C., 26.1 cm. at 25°C., 76 cm. at 56.9°C. (12), 1.966 cm. at −25°C., 4.646 cm. at −10°C., 7.802 cm. at 0°C., 12.59 cm. at 10°C., 29.499 cm. at 30°C., 60.746 cm. at 50°C., 83.723 cm. at 60°C., 97.274 cm. at 65°C. (272), 77 mm. at 0°C., 98 mm. at 5°C., 124 mm. at 10°C., 153 mm.

at 15°C., 191 mm. at 20°C., 235 mm. at 25°C., 287 mm. at 30°C., 346 mm. at 35°C., 419 mm. at 40°C., 501 mm. at 45°C., 599 mm. at 50°C., 709 mm. at 55°C., 839 mm. at 60°C. (165), 238.3 mm. at 25°C. (368). Its critical temperature is 213.8°C. (269), 221°C. (128), 230°C. (203), 233.6°C. (247).

The heat of fusion of silicon tetrachloride is 10.85 cal. per gram at -70.3°C. (181). Its heat of vaporization is 6.3 Cal. per mole (238) or 7.19 Cal. per mole (326). Its heat of formation is as follows (24, 338):

$$\mathrm{Si_{cryst}} + 4\mathrm{HCl} \rightarrow \mathrm{SiCl_{4\,gas}} + 121.8\ \mathrm{Cal.}$$

$$\mathrm{Si_{cryst}} + 4\mathrm{HCl} \rightarrow \mathrm{SiCl_{4\,liq.}} + 128.1\ \mathrm{Cal.}$$

The calculated value in the latter case is 154 Cal. (283). The temperatures of formation of silicon tetrachloride from silicon dioxide, chlorine, and carbon are 740°C. from amorphous silicon dioxide, 1060°C. from tridymite or cristobalite, and 1220°C. from quartz (122).

The coefficient of thermal expansion of silicon tetrachloride at 20°C. is 0.001430 (251) or 0.001446 (333); between 25° and 30°C. it is 0.0014124 (277). Its specific heat is 0.1904 between 10° and 15°C. (238, 272), 0.1904 between 20° and 40°C. (161), 0.1322 between 90° and 234°C. (272). Its index of refraction has been reported as follows: 1.404 for red light (107); H_α, 1.4119 (red ray); H_β, 1.4200 (green ray); H_γ, 1.4244 (violet ray) (131); 1.41019 for the H_α-ray; 1.41829 for the H_β-ray; 1.41257 for the D-ray; 1.42306 for the H_γ-ray (1). For rays of wave length $\lambda = 226$, 394, and 589 $\mu\mu$, the index of refraction = 1.50823, 1.43334, and 1.4182, respectively (325). The beginning of continuous absorption in the spectra of the hot vapors was determined as λ 2500 for silicon tetrachloride (71). Bergmann and Engel (22) determined from the dipole moment ($SiCl_4 = 0$) and from the spatial structure that silicon tetrachloride is a regular tetrahedron. The dielectric constant was found to be 2.40 by Schundt (305) at 16°C. with wave length $\lambda = 80$ cm. Schuster (306), by the use of an equation derived from Stefan's equation and the Clausius–Clapeyron equation, calculated the internal pressure of silicon tetrachloride as 1184. The solubility of iodine in silicon tetrachloride, expressed as mole per cent, is 0.1713 at 0.10°C., 0.4987 at 25°C., and 0.8801 at 40°C. (232). Biltz and Keunecke (30) found that anhydrous liquid hydrogen sulfide at -78.5°C. dissolves silicon tetrachloride without discontinuity in the isothermal vaporization curve. Wood (368) determined the fugacity of silicon tetrachloride as 234.5 at 25°C. Taylor and Hildebrand (330) found that at 0°C. 0.131 g. of chlorine dissolves in 1 g. of silicon tetrachloride. Biltz and Meinecke (31) found the freezing point curves of mixtures of silicon tetrachloride and chlorine to have a eutectic at -117°C. with 86 per cent of chlorine. Besson (28) observed that silicon tetrachloride does not absorb phosphine at ordinary temperature, but that it dissolves twenty times its volume at −20°C. and forty times its volume at −50°C. The conduction of a saturated solution of silicon tetrachloride in liquid hydrogen sulfide = 0.129 ($\lambda \times 10^6$) (268). The compressibility of silicon tetrachloride in reciprocal atmospheres at 25°C. is 1652 (142). Its thermal pressure coefficient (atm. × liters^2 per mole of liquid) is 34.00 (142).

Chemical properties

(*1*) *Action with hydrogen and oxygen.* When a mixture of silicon tetrachloride vapor and hydrogen is heated to redness, siliconchloroform is produced (100); when a mixture of the tetrachloride vapor and dry oxygen or air is heated, an oxychloride, $2Si_2OCl_6$, is obtained (100). Troost and Hautefeuille (340) obtained the same oxychloride by passing silicon tetrachloride through a heated porcelain tube with or without a packing of fragments of feldspar or alkali silicates.

(*2*) *Action with water.* According to Berzelius (27) silicon tetrachloride first floats on the surface of water and then dissolves with decomposition, forming hydrated silica and hydrogen chloride. Silicon tetrachloride and water form metasilicic acid (327). At a red heat Daubrée (69) found that water vapor and silicon tetrachloride produced crystals of silicon dioxide. Schwarz and Liede (308) obtained the α-acid by the hydrolysis of silicon tetrachloride at 100°C.

(*3*) *Action with ammonia, hydrazine, and sodamide.* Gaseous ammonia reacts with silicon tetrachloride alone or dissolved in benzene, forming silicontetramide (183). By saturating silicon tetrachloride with dry ammonia a white mass of silicon hexamminotetrachloride, $SiCl_4 \cdot 6NH_3$, is formed (37); upon passing gaseous ammonia into a solution of silicon tetrachloride in benzene in an atmosphere of dry nitrogen a product was obtained approximating silicon octamminotetrachloride, $SiCl_4 \cdot 8NH_3$ (183). Lay (182) found that with hydrazine a white, fuming compound, probably silicon tetrahydrazinetetrachloride, $SiCl_4 \cdot 4N_2H_4$, is formed by the action of a benzene solution of silicon tetrachloride on an emulsion of hydrazine in benzene; he also showed that the tetrachloride reacts with sodamide at 150°C., forming silicon and a sublimate of ammonium chloride and silicon tetraamminotetrachloride.

(*4*) *Action with acids and acid anhydrides.* Hydrogen iodide and silicon tetrachloride vapor at a dull red heat produce a mixture of chloroiodides (28). Hydrogen sulfide does not act on silicon tetrachloride at ordinary temperature, but at red heat silicon tetrahydrosulfide is formed (100, 130).

Concentrated sulfuric acid, decomposes silicon tetrachloride into silicon dioxide and hydrogen chloride (309). Chlorosulfonic acid decomposes silicon tetrachloride in the presence of sunlight or at 170°C: (60). Neither nitric acid nor aqua regia unites with silicon tetrachloride (354). Nitrous acid was found by Weber (354) to react with silicon tetrachloride to form nitrosyl chloride. Butyric acid when heated with silicon tetrachloride in a sealed tube to 150–160°C. forms butyl chloride (270). Montonna (223) prepared chlorides of acetic, propionic, butyric, isobutyric, benzoic, phenylacetic, and sebacic acids by heating the respective acid with silicon tetrachloride.

At red heat phosphorus pentoxide reacts with silicon tetrachloride to form oxychlorides of phosphorus (100, 270). When pure melted sulfur trioxide is mixed with silicon tetrachloride, a mere solution is formed at first, but on standing a reaction takes place, very slowly in the cold and more rapidly if the mixture is heated to 50°C. This reaction produces probably a mixture of $S_2O_5Cl_2$ and Si_2OCl_6 (295). Gustavson (129) formed pyrosulfuryl chloride by the reaction of sulfur trioxide with silicon tetrachloride.

(*5*) *Action with halogens and halogen salts.* Moissan (221) found that arsenic trifluoride reacts in the cold with silicon tetrachloride, forming silicon tetrafluoride and arsenic trichloride. Hollemann and Slijper (145) found that sodium fluoride reacts with silicon tetrachloride, forming sodium chloride and silicon tetrafluoride.

(*6*) *Action with silicon and carbon.* When silicon tetrachloride vapor was passed over heated silicon Troost and Hautefeuille (340) obtained a subchloride. Ruff (286) found that silicon tetrachloride is not affected by carbon at high temperature, while Pring and Fielding (263) observed the formation of silicon carbide in the presence of hydrogen at 1700°C.

(*7*) *Action with metals.* When potassium is heated in the vapor of silicon tetrachloride the metal burns, forming potassium chloride and silicon; if molten potassium is dropped into liquid silicon tetrachloride an explosion results. Sodium, zinc, and silver at a red heat withdraw the chlorine from silicon tetrachloride without forming higher chlorides (18, 100); Rauter (270) found that zinc, aluminum, beryllium, and magnesium react at 200–300°C., forming the metal chloride and silicon. Parravano and Mazzetti (248) found that silicon tetrachloride reacts with iron at 900°C., forming an iron silicide. Vigouroux (343) showed that, with reduced iron at dull red heat, iron silicide and ferrous chloride are formed; cobalt and nickel react similarly.

(*8*) *Action with metal oxides.* Rauter (270) found that most metal oxides react with silicon tetrachloride, forming the metal chloride or oxychloride and silica. Sodium oxide reacts with silicon tetrachloride at red heat, forming sodium silicate and sodium chloride (100).

(*9*) *Action with salts.* At ordinary temperatures lead thiocyanate reacts with silicon tetrachloride to form silicon tetrathiocyanate (100). Montonna (223) prepared the anhydride of acetic acid by heating anhydrous sodium acetate with silicon tetrachloride.

(*10*) *Miscellaneous reactions.* Phärmazeutische Industrie and Hauschka

(25) obtained Austrian patent 86,131 for the preparation, from guaiacol and silicon tetrachloride, of dichlorodiguaiacolsilicomethane, $SiCl_2(OC_6H_4OCH_3)_2$, and tetraguaiacolsilicomethane, $Si(OC_6H_4OCH_3)_4$.

Rosenheim and Sorge (282) from an ethereal solution of 1 mole of silicon tetrachloride and 3 moles of pyrocatechol obtained a mass of very deliquescent, white crystals which gave off hydrogen chloride; from the condensed ethyl alsohol solution of these, alcoholic ammonia precipitated ammonium tripyrocatecholsilicate, $C_6H_4O{=}Si(OC_6H_4ONH_4)_2$, white crystals. Similarly, an alcoholic solution of pyridine gives the pyridinium salt, which forms bright yellow prisms.

By the action of silicon tetrachloride on dry acetone, Currie (66) obtained a jelly-like mass which, upon stirring with water, gave mesityl oxide.

From an ether solution of silicon tetrachloride, treated in the cold with an ethereal solution of ethylmagnesium bromide and then refluxed for 3 to 4 hr., Martin and Kipping (193) by careful fractionating obtained ethylsilicon trichloride, b.p. 100°C., diethylsilicon dichloride, b.p. 128–130°C., and triethylsilicyl chloride, b.p. 143°C.

REFERENCES

(1) ABATI: Gazz. chim. ital. **27**, II, 437–55 (1897).
(2) AESCHLIMANN: J. Chem. Soc. **1927**, 413–17.
(3) AESCHLIMANN AND MCCLELAND: J. Chem. Soc. **125**, 2025–35 (1924).
(4) ARII: Bull. Inst. Phys. Chem. Research (Tokyo) **8**, 714–18 (1929).
(5) ARMSTRONG: J. Chem. Soc. **29**, 173–6 (1871).
(6) BARTON: Chem. Abstracts **10**, 1584 (1916).
(7) BAUDRIMONT: J. pharm. chim. [4] **40**, 161 (1871).
(8) BAUER AND STOCKHAUSEN: J. prakt. Chem. **130**, 35–44 (1931).
(9) BAUMSTARK: Ann. **140**, 75–86 (1866).
(10) BAXTER, BEZZENBERGER, AND WILSON: J. Am. Chem. Soc. **42**, 1386–93 (1920).
(11) BAXTER, WEATHERILL, AND HOLMES: J. Am. Chem. Soc. **42**, 1194–7 (1920).
(12) BECKER AND MEYER: Z. anorg. Chem. **43**, 251–66 (1905).
(13) BECKURTZ AND OTTO: Ber. **11**, 2058–61 (1878).
(14) BECKURTZ AND OTTO: Ber. **11**, 2061–6 (1878).
(15) BEDSON: Ann. **180**, 235–9 (1876).
(16) BEHREND: Ber. **8**, 1004–5 (1875).
(17) BEHREND: J. prakt. Chem. [2] **15**, 23 (1877).
(18) BEKETOFF: Bull. soc. chim. [1] **1**, 22 (1859).
(19) BELOGLAZOV: Contributions to the Study of the Natural Resources of the U. S. S. R., No. **56**, 20–3 (1926).
(20) BENRATH: Z. wiss. Phot. **14**, 217 (1915).
(21) BENRATH AND OBLADEN: Z. wiss. Phot. **22**, 65 (1922).
(22) BERGMANN AND ENGEL: Z. physik. Chem. **13**, 332–46 (1931).
(23) BERT: Bull. soc. chim. **31**, 1264–70 (1922).
(24) BERTHOLET: Ann. chim. phys. [5] **15**, 213–20 (1878).
(25) BERTRAND: Bull. soc. chim. [2] **33**, 565 (1880).
(26) BERZELIUS: Pogg. Ann. **1**, 169–230 (1824).
(27) BERZELIUS: Pogg. Ann. **2**, 210–18 (1824).

(28) Besson: Compt. rend. **112**, 611–14 (1891).
(29) Billitz and Heumann: Ber. **16**, 483–5 (1883).
(30) Biltz and Keunecke: Z. anorg. Chem. **147**, 171–87 (1925).
(31) Biltz and Meinecke: Z. anorg. Chem. **131**, 1–21 (1923).
(32) Blanchard: Bull. soc. chim. **45**, 1194–204 (1928).
(33) Blicke and Oakdale: J. Am. Chem. Soc. **54**, 2993–6 (1932).
(34) Blicke and Oneto: J. Am. Chem. Soc. **57**, 749–53 (1935).
(35) Blicke and Powers: J. Am. Chem. Soc. **54**, 3353–60 (1932).
(36) Blicke and Smith: J. Am. Chem. Soc. **52**, 2946–51 (1930).
(37) Blix and Wirbelauer: Ber. **36**, 4220–8 (1903).
(38) Böck and Moser: Monatsh. **34**, 1825 (1913).
(39) Bond and Beach: J. Am. Chem. Soc. **48**, 348–56 (1926).
(40) Bond and Stephens: J. Am. Chem. Soc. **51**, 2910–22 (1929).
(41) Boulin and Simon: Compt. rend. **169**, 338–41 (1919).
(42) Bourion: Compt. rend. **145**, 62–4 (1907).
(43) Brallier: Trans. Electrochem. Soc. **49**, 257–63 (1926).
(44) Briggs: Chem. Zentr. [4] **93**, 699 (1922).
(45) Budnikov and Shilov: Mitt. wiss-tech. Arb. Rep. (Russia) **13**, 64–5 (1924).
(46) Budnikov and Shilov: Z. angew. Chem. **39**, 765 (1926).
(47) Buff and Wöhler: Ann. **104**, 94–109 (1857).
(48) Burkhardt: J. Chem. Soc. **1933**, 337–8.
(49) Burrows and Turner: J. Chem. Soc. **117**, 1373–83 (1920).
(50) Burrows and Turner: J. Chem. Soc. **119**, 426–37 (1921).
(51) Burton and Gibson: J. Chem. Soc. **1926**, 464–70.
(52) Carrara: Gazz. chim. ital. **31**, i, 450 (1901).
(53) Challenger and Pritchard: J. Chem. Soc. **125**, 864–75 (1924).
(54) Challenger and Ridgway: J. Chem. Soc. **121**, 104–20 (1922).
(55) Claesson: J. prakt. Chem. [2] **19**, 231–65 (1878).
(56) Claesson: J. prakt. Chem. [2] **20**, 1–34 (1879).
(57) Clausnizer: Ber. **11**, 2007–9 (1878).
(58) Clausnizer: Ber. **11**, 2009–11 (1878).
(59) Clausnizer: Ber. **11**, 2011–12 (1878).
(60) Clausnizer: Ann. **196**, 265–98 (1879).
(61) Colson: Compt. rend. **115**, 657–9 (1892).
(62) Consortium für Elektrochemische Industrie-ges.: Chem. Abstracts **17**, 857 (1923).
(63) Corbellini: Giorn. chim. ind. applicata **9**, 118–20 (1927).
(64) Corbellini: Giorn. chim. ind. applicata **9**, 365–7 (1927).
(65) Corbellini and Albenga: Gazz. chim. ital. **61**, 111–30 (1931).
(66) Currie: J. Am. Chem. Soc. **35**, 1061 (1913).
(67) Dachlauer: Chem. Zentr. **103**, 2076 (1932).
(68) Daubrée: Ann. Mines [4] **19**, 684 (1851).
(69) Daubrée: Compt. rend. **39**, 135–40 (1854).
(70) Davis: J. Chem. Soc. **89**, 1575–8 (1906).
(71) Deb: Bull. Acad. Sci. United Provinces Agra Oudh, India **1**, 92–9 (1931–32).
(72) DeCarli: Atti. congr. naz. chim. pura applicata **1923**, 399.
(73) Dehn: Am. Chem. J. **40**, 80–127 (1908).
(74) Dehn and Wilcox: Am. Chem. J. **35**, 1–54 (1906).
(75) Demarçay: Compt. rend. **80**, 51–3 (1875).
(76) Demoly: Compt. rend. trav. chim. **5**, 325 (1849).
(77) Dermer and Fernelius: Z. anorg. allgem. Chem. **221**, 83–96 (1934).

(78) DEVILLE: Ann. chim. phys. [3] **43**, 5–33 (1855).
(79) DEWAR AND CRANSTON: Chem. News **20**, 174–5 (1869).
(80) DEWAR AND CRANSTON: Bull. soc. chim. [2] **13**, 131 (1870).
(81) DIDIER: Compt. rend. **101**, 882–4 (1885).
(82) DILTHEY: Ann. **344**, 300–42 (1906).
(83) DUMAS: Ann. chim. phys. [2] **33**, 265–71 (1826).
(84) DUMAS: J. pharm. chim [1] **12**, 300 (1826).
(85) DUPPA: Compt. rend. **42**, 352–4 (1856).
(86) EBELMEN: J. pharm. chim. [3] **12**, 437 (1846).
(87) EBELMEN: Ann. chim. phys. [3] **16**, 129-66 (1846).
(88) ELLIS: Chem. News **95**, 122–3 (1907).
(89) EMICH: Ber. **28**, 1585 (1895).
(90) ERDMAN: Ber. **26**, 1990–4 (1893).
(91) EVARD: Compt. rend. **196**, 2007–9 (1933).
(92) FAURE: Compt. rend. **107**, 339–40 (1888).
(93) FAVRE: Chem. Abstracts **30**, 8541 (1936).
(94) FEGLER: Compt. rend. soc. biol. **100**, 218–21 (1929).
(95) FLEURY: Bull. soc. chim. **27**, 699–704 (1920).
(96) FLURY: Z. expt. Med. **13**, 523–78 (1921).
(97) FRIEDEL AND CRAFTS: Ann. chim. phys. [4] **9**, 5–51 (1866).
(98) FRIEDEL AND GUÉRIN: Compt. rend. **82**, 509–12 (1876).
(99) FRIEDEL AND LADENBURG: Ann. **143**, 118–28 (1867).
(100) FRIEDEL AND LADENBURG: Ann. **203**, 241–55 (1880).
(101) FRIES AND WEST: Chemical Warfare. McGraw-Hill Book Co., Inc., New York (1931).
(102) FUCHS AND KATSCHER: Ber. **60**, 2288–96 (1927).
(103) FUCHS AND KATSCHER: Ber. **62**, 2381–6 (1929).
(104) FUCHS AND KATSCHER: Chem.-Ztg. **101**, 3460 (1930).
(105) GARDNER AND SUGDEN: J. Chem. Soc. **1929**, 1298–302.
(106) GATTERMANN: Ber. **22**, 186-97 (1889).
(107) GATTERMANN AND WEINLIG: Ber. **27**, 1943–8 (1894).
(108) GEBAUER-FUELNEGG AND HAEMERLE: J. Am. Chem. Soc. **53**, 2648–53 (1931).
(109) GEBAUER-FUELNEGG AND JARSCH: J. Am. Chem. Soc. **52**, 2451–4 (1930).
(110) GEBAUER-FUELNEGG AND JARSCH: Monatsh. **56**, 317–21 (1930).
(111) GEORGE: Ann. Phil. **9**, 18 (1825).
(112) GEUTHER: Ber. **5**, 925 (1872).
(113) GIBSON AND JOHNSON: J. Chem. Soc. **1928**, 92–9.
(114) GIBSON, JOHNSON, AND VINING: Rec. trav. chim. **49**, 1006–35 (1930).
(115) GIBSON AND SMILES: J. Chem. Soc. **123**, 2388–93 (1923).
(116) GILCHRIST AND MATZ: Med. Bull. Veterans' Admin. **10**, 79–98 (1933).
(117) GILMAN, BURTNER, CALLOWAY, AND TURCK: J. Am. Chem. Soc. **57**, 907–8 (1935).
(118) GLADSTONE: J. Chem. Soc. **59**, 290–326 (1891).
(119) GOERGES AND STÄHLER: Ber. **42**, 3200–18 (1909).
(120) GREY AND PATTERSON: Smoke—A Study in Aerial Disperse Systems. Edward Arnold and Co., London (1932).
(121) GRÜN AND WETTERKAMP: Z. Farben-Ind. **7**, 375 (1909).
(122) GRUNER AND ELÖD: Z. anorg. allgem. Chem. **195**, 269–87 (1931).
(123) GRUTTNER AND KRAUSE: Ber. **49**, 437–44 (1916).
(124) GRUTTNER AND WIERNIK: Ber. **48**, 1473–86 (1915).
(125) GRYSZKIEWITCZ-TROCHIMOWSKI, MATEYAK, AND ZABLOTSKI: Bull. soc. chim. [4] **41**, 1323–33 (1927).

(126) Gryszkiewicz-Trochimowski and Sikorski: Bull. soc. chim. [4] **41**, 1570–85 (1927).
(127) Guldberg: Christiana Vet. Förh., p. 20 (1882).
(128) Guldberg: Z. physik. Chem. **5**, 374–82 (1890).
(129) Gustavson: Ber. **5**, 332 (1872).
(130) Gustavson: Ann. chim. phys. [5] **2**, 200–25 (1874).
(131) Haagen: Pogg. Ann. **131**, 117–28 (1867).
(132) Haase: Ber. **26**, 1052–4 (1893).
(133) Hampe: Ann. **126**, 43–8 (1863).
(134) Hanzlik and Tarr: J. Pharmacol. **14**, 221–8 (1919).
(135) Hautefeuille: Bull. soc. chim. [2] **23**, 289 (1875).
(136) Haworth and Lapworth: J. Chem. Soc. **125**, 1299–307 (1924).
(137) Hempel and von Haasy: Z. anorg. Chem. **23**, 32–42 (1900).
(138) Henley and Sugden: J. Chem. Soc. **1929**, 1058–65.
(139) Henley and Turner: J. Chem. Soc. **1931**, 1172–81.
(140) Heumann and Köchlin: Ber. **15**, 416–20 (1882).
(141) Heumann and Köchlin: Ber. **15**, 1114–19 (1882).
(142) Hildebrand and Carter: J. Am. Chem. Soc. **54**, 3592–603 (1932).
(143) Hock and Knauff: Z. anorg. allgem. Chem. **228**, 193–9 (1936).
(144) Holleman and Caland: Ber. **44**, 2504–22 (1911).
(145) Hollemann and Slijper: Rec. trav. chim. **23**, 380 (1904).
(146) Höltje: Z. anorg. allgem. Chem. **190**, 241–56 (1930).
(147) Hunt and Turner: J. Chem. Soc. **127**, 996–9 (1925).
(148) Hunter: J. Am. Chem. Soc. **32**, 330–6 (1910).
(149) Hutchins: Chem. Abstracts **12**, 1500 (1918).
(150) Hutchins: Trans. Electrochem. Soc. **35**, 309–20 (1919).
(151) Hutchins: Chem. Abstracts **12**, 1914 (1918).
(152) Ingersoll: J. Optical Soc. Am. **6**, 663–81 (1922).
(153) Ipatiev, Razubaiev, and Stromski: Ber. **62**, 598–604 (1929).
(154) Jackson: Chem. Rev. **17**, 251–5 (1935).
(155) Jackson: Chem. Rev. **17**, 257–60 (1935).
(156) Jackson: Chem. Rev. **17**, 260–9 (1935).
(157) Johnson: Ber. **65**, 294–302 (1932).
(158) Johnson and Smiles: J. Chem. Soc. **123**, 2384–8 (1923).
(159) Jones, Dykes, Davis, Griffiths, and Webb: J. Chem. Soc. **1932**, 2284–93.
(160) Jüngst and Mews: J. Chem. Soc. **88**, 316 (1905).
(161) Kahlenberg and Koenig: J. Phys. Chem. **12**, 290 (1908).
(162) Karantassis: Compt. rend. **194**, 461 (1932).
(163) Kashtanov: J. Gen. Chem. (U. S. S. R.) **4**, 1204–5 (1934).
(164) Katscher, Lehr, Harnisch, and Steinhardt: Monatsh. **56**, 381–90 (1930).
(165) Kearby: J. Am. Chem. Soc. **58**, 374–5 (1936).
(166) Kharasch: Chem. Zentr. **97**, 1692 (1926).
(167) Kipping and Thompson: J. Chem. Soc. **1928**, 1137.
(168) Klages and Vollberg: Chem. Abstracts **6**, 671 (1912).
(169) König and von der Pfordten: Ber. **22**, 1485–94 (1889).
(170) Köster: Jahresber. **6**, 120 (1826).
(171) Kowalewsky: Z. anorg. Chem. **25**, 189–95 (1901).
(172) Kraft and Alekseev: J. Gen. Chem. (U. S. S. R.) **2**, 726–9 (1932).
(173) Krajčinovič: Ber. **59**, 2117–19 (1926).
(174) Krajčinovič: Ber. **62**, 579–81 (1929).
(175) Krajčinovič: Ber. **63**, 2276–8 (1930).
(176) Krajčinovič: Arhiv. Hem. Farm. **5**, 2–13 (1931).

(177) Kretov and Berlin: J. Gen. Chem. (U. S. S. R.) **1**, 411–18 (1931).
(178) Krummenacher: Chem. Abstracts **27**, 2765 (1933).
(179) Lacoste and Michaelis: Ber. **11**, 1883–7 (1878).
(180) Lacoste and Michaelis: Ann. **201**, 184–261 (1880).
(181) Latimer: J. Am. Chem. Soc. **44**, 90–7 (1922).
(182) Lay: Ueber Silicum, Stickstoff, Wasserstoff Verbindungen. Thesis, München, 1910.
(183) Lengfeld: Am. Chem. J. **21**, 531–9 (1899).
(184) Lepin: J. Russ. Phys. Chem. Soc. **52**, 1–17 (1920).
(185) Levaillant and Simon: Compt. rend. **169**, 140–3 (1919).
(186) Levaillant and Simon: Compt. rend. **169**, 234–7 (1919).
(187) Luchinskiĭ and Al'tman: Z. anorg. allgem. Chem. **225**, 321–6 (1935).
(188) Lumière, Lumière, and Perrin: Bull. soc. chim. [3] **29**, 1228–9 (1903).
(189) Lustig and Katscher: Monatsh. **48**, 87–98 (1927).
(190) Lutschinsky: Z. physik. Chem. **169**, 269–74 (1934).
(191) Malinovskiĭ: J. Gen. Chem. (U. S. S. R.) **5**, 1355–8 (1935).
(192) Martin: J. Chem. Soc. **105**, 2836–60 (1914).
(193) Martin and Kipping: J. Chem. Soc. **95**, 302–14 (1912).
(194) Matignon and Bourion: Compt. rend. **138**, 631–63 (1904).
(195) Matossi and Aderhold: Z. Physik **68**, 683–95 (1931).
(196) Matthews: J. Phys. Chem. **9**, 641 (1905).
(197) McCleland and Whitworth: J. Chem. Soc. **1927**, 2753–7.
(198) McInerny, Williams, and Glaze: Chem. Abstracts **27**, 1460 (1933).
(199) McIntosh: J. Am. Chem. Soc. **27**, 1013–16 (1905).
(200) McKee and Salls: Chem. Abstracts **19**, 3492 (1925).
(201) McKenzie and Wood: J. Chem. Soc. **117**, 406–15 (1920).
(202) Melsens: Compt. rend. **76**, 92–4 (1873).
(203) Mendeleeff: Compt. rend. **51**, 97–9 (1860).
(204) Merz: J. prakt. Chem. [1] **99**, 162 (1866).
(205) Meyer: Z. anorg. allgem. Chem. **203**, 146–55 (1931).
(206) Michaelis: Z. Chem. [2] **6**, 460 (1870).
(207) Michaelis: Jena Z. **6**, 79 (1871).
(208) Michaelis: Z. Chem. Phys. Math. [2] **7**, 149 (1871).
(209) Michaelis: Ber. **8**, 1316–7 (1875).
(210) Michaelis: Ber. **9**, 1566–9 (1876).
(211) Michaelis: Ber. **10**, 622–7 (1877).
(212) Michaelis: Ann. **320**, 271–344 (1902).
(213) Michaelis: Ann. **321**, 141–248 (1902).
(214) Michaelis and Link: Ann. **207**, 193–219 (1881).
(215) Michaelis and Loesner: Ber. **27**, 263–72 (1894).
(216) Michaelis and Reese: Ber. **15**, 2876–7 (1882).
(217) Michaelis and Schifferdecker: Ber. **6**, 996–9 (1873).
(218) Michaelis and Schulte: Ber. **14**, 912–14 (1881).
(219) Mills and Robinson: J. Chem. Soc. **1927**, 1823–32.
(220) Miquel: Bull. soc. chim. [2] **26**, 501 (1876).
(221) Moissan: Ann. chim. phys. [6] **19**, 280–6 (1890).
(222) Montemartini and Losana: Giorn. chim. ind. applicata **5**, 487–95 (1923).
(223) Montonna: J. Am. Chem. Soc. **49**, 2114–16 (1927).
(224) Moore: Chem. Abstracts **14**, 3300 (1920).
(225) Morgan and Vining: J. Chem. Soc. **117**, 777–83 (1920).
(226) Moureu: Bull. soc. chim. [3] **11**, 767 (1894).
(227) Müller: Ber. **6**, 227–31 (1873).

(228) Naik and Amin: J. Indian Chem. Soc. **5,** 579–83 (1928).
(229) Nakrav: Chem. Abstracts **31,** 2370 (1937).
(230) Nametkin and Nekrasov: Z. anal. Chem. **77,** 285–9 (1929).
(231) Nasu: Bull. Chem. Soc. Japan **9,** 198–205 (1934).
(232) Negishi, Donnally, and Hildebrand: J. Am. Chem. Soc. **55,** 4793–800 (1923).
(233) Nenitzescu and Isacescu: Ber. **67,** 1391–3 (1934).
(234) Oberhauser: Ber. **60B,** 1434–9 (1927).
(235) Odling: A Manual of Chemistry, London, **1,** 163 (1861).
(236) Oersted: Pogg. Ann. **5,** 132 (1825).
(237) Oeschslin: Chem. Zentr. **93,** 945 (1922).
(238) Ogier: Ann. chim. phys. [5] **20,** 5–66 (1880).
(239) Ogier: Compt. rend. **96,** 646–9 (1883).
(240) Oreshkin: Contributions to the Study of the Natural Resources of the U. S. S. R., No. **56,** 14–20 (1926).
(241) Orlowsky: Ber. **8,** 332–5 (1875).
(242) Pacsu: J. Am. Chem. Soc. **52,** 2563–7 (1930).
(243) Pacsu: J. Am. Chem. Soc. **52,** 2568–71 (1930).
(244) Pacsu: J. Am. Chem. Soc. **52,** 2571–5 (1930).
(245) Palmer and Adams: J. Am. Chem. Soc. **44,** 1356–82 (1922).
(246) Pamfilov and Shtandel: J. Gen. Chem. (U. S. S. R.) **7,** 258–61 (1937).
(247) Parker and Robinson: J. Chem. Soc. **1927,** 2977–81.
(248) Parravano and Mazzetti: Rec. trav. chim. **42,** 821 (1923).
(249) Persoz: Ann. chim. phys. [2] **44,** 321 (1830).
(250) Pharmazeutiche Industrie and Hauschka: Chem. Abstracts **17,** 1865 (1923).
(251) Pierre: Ann. chim. phys. [3] **20,** 5–53 (1847).
(252) Pollak and Gebauer-Fuelnegg: Monatsh. **46,** 499–514 (1926).
(253) Pollak and Gebauer-Fuelnegg: Monatsh. **47,** 109–18 (1926).
(254) Pollak and Gebauer-Fuelnegg: Monatsh. **47,** 537–58 (1926).
(255) Pollak, Gebauer-Fuelnegg, and Blumenstock-Halward: Monatsh. **49,** 187–202 (1928).
(256) Pollak, Gebauer-Fuelnegg, and Riesz: Monatsh. **46,** 383–97 (1926).
(257) Pollak, Heimberg-Krauss, Katscher, and Lustig: Monatsh. **55,** 358–78 (1930).
(258) Pomeranz: Seifensieder-Ztg. **59,** 3 (1932).
(259) Pomeranz: Seifensieder-Ztg. **59,** 79–81 (1932).
(260) Pope and Turner: J. Chem. Soc. **117,** 1447–52 (1920).
(261) Prentiss: Chemicals in War. McGraw-Hill Book Co., New York (1937).
(262) Priesz: German patents 334,248; 334,249 (1917).
(263) Pring and Fielding: J. Chem. Soc. **95,** 1497–1506 (1909).
(264) Prinz: Ann. **223,** 371–8 (1884).
(265) Pytasz and Rabek: Przemysl Chem. **14,** 529–35 (1930).
(266) Quick and Adams: J. Am. Chem. Soc. **44,** 805–16 (1922).
(267) Railton: J. Chem. Soc. **7,** 180–4 (1855).
(268) Ralston and Wilkinson: J. Am. Chem. Soc. **50,** 258–64 (1928).
(269) Ramsay and Shields: Z. physik. Chem. **12,** 433–75 (1893).
(270) Rauter: Ann. **270,** 235–66 (1892).
(271) Regnault: Ann. chim. phys. [3] **1,** 129–207 (1841).
(272) Regnault: Compt. rend. **36,** 676–87 (1853).
(273) Renz: Ber. **39,** 249–50 (1906).
(274) Reynolds: J. Proc. Roy. Soc. N.S. Wales **66,** 167–70 (1932).
(275) Richter: Trans. Electrochem. Soc. **35,** 323–33 (1919).
(276) Roberts, Turner, and Bury: J. Chem. Soc. **1926,** 1443–7.

(277) Robinson and Smith: J. Chem. Soc. **1926,** 1262–82.
(278) Roeder and Blase: Ber. **47,** 2748–52 (1914).
(279) Rose: Ann. **40,** 240 (1841).
(280) Rosenheim and Schütte: Z. anorg. Chem. **26,** 239–57 (1901).
(281) Rosenheim, Schnabel, and Bilecki: Ber. **48,** 447–52 (1915).
(282) Rosenheim and Sorge: Ber. **53B,** 932–9 (1920).
(283) Roth and Becker: Z. physik. Chem. **A159,** 1–26 (1932).
(284) Ruff: Ber. **34,** 3509–15 (1901).
(285) Ruff: Ber. **37,** 4513–21 (1905).
(286) Ruff: Ber. **43,** 1564–74 (1910).
(287) Ruff and Albert: Ber. **38,** 53–64 (1905).
(288) Ruff and Ipsen: Ber. **36,** 1777–83 (1903).
(289) Ruff and Neuman: Z. anorg. allgem. Chem. **128,** 81–95 (1923).
(290) Saccharin-Fabrik Aktiengesellschaft vorm Fahlberg, List & Co.: Chem. Abstracts **5,** 2160 (1911).
(291) Saccharin-Fabrik Aktiengesellschaft vorm Fahlberg, List & Co.: Chem. Abstracts **5,** 2693 (1911).
(292) Sagawa: Complete Abstracts of Japanese Chemical Literature **6,** 341 (1932).
(293) Sanger and Riegel: Z. anorg. Chem. **76,** 79–128 (1912).
(294) Sanger and Riegel: Proc. Am. Acad. Arts Sci. **47,** 673–718 (1912).
(295) Sanger and Riegel: Proc. Am. Acad. Arts Sci. **48,** 573–95 (1913).
(296) Sankyô Joint Stock Company: Chem. Abstracts **12,** 518 (1918).
(297) Scagliarini and Tartarni: Atti. accad. Lincei [6] **4,** 318–24 (1926).
(298) Schedler and Marchant: Chem. Abstracts **14,** 97 (1920).
(299) Schenk: Pharm. Ztg. **54,** 592–3 (1909).
(300) Schmidt: Ber. **58B,** 400–4 (1925).
(301) Schmidt, Steindorff, Fluss, and Schaffrath: Chem. Zentr. **97,** 2046 (1926).
(302) Schneider: Z. anorg. Chem. **8,** 81–97 (1895).
(303) Schnitzler: Dingler's J. **21,** 485 (1874).
(304) Schulte: Ber. **15,** 1955–60 (1882).
(305) Schundt: J. Phys. Chem. **8,** 122 (1904).
(306) Schuster: Z. anorg. allgem. Chem. **146,** 299–304 (1925).
(307) Schuster: Compt. rend. **195,** 611–14 (1932).
(308) Schwartz and Liede: Ber. **53B,** 1680–9 (1920).
(309) Sérullas: J. chim. med. **8,** 3 (1832).
(310) Sherlin and Yakubovich: J. prakt. Chem. **138,** 23–41 (1933).
(311) Sherlin and Yakubovich: Bull. soc. chim. [5] **1,** 1367–73 (1934).
(312) Société des Produits Chim. de Saint-Bueil: Chem. Abstracts **31,** 4065 (1937).
(313) Société pour l'Industrie Chimique à Bale: Chem. Zentr. **104, II,** 1413 (1933).
(314) Stähler and Bachran: Ber. **44,** 2906–15 (1911).
(315) Stähler and Wirtwein: Ber. **38,** 2619–30 (1905).
(316) Staudinger and Bruson: Ann. **447,** 110–22 (1926).
(317) Steindorff and Schwabe: Chem. Zentr. **101,** 2298 (1930).
(318) Steinkopf and Dudek: Ber. **62,** 2494–7 (1929).
(319) Steinkopf, Dudek, and Schmidt: Ber. **61,** 1911–18 (1928).
(320) Steinkopf, Schubart, and Schmidt: Ber. **61,** 678–82 (1928).
(321) Steinkopf and Schmidt: Ber. **61,** 675–8 (1928).
(322) Steinkopf, Schmidt, and Penz: J. prakt. Chem. **141,** 301–5 (1934).
(323) Steinkopf and Schwen: Ber. **54,** 1437–65 (1921).

(324) Steinkopf and Smie: Ber. **59,** 1453-63 (1926).

(325) Stiefelhagen: Dispersion flüssiger Trichloride und Tetrachloride für ultraviolette Strahlen. Thesis, Berlin, 1905.

(326) Stock, Somieski, and Wintgen: Ber. **50,** 1754-64 (1917).

(327) Stock and Zeidler: Ber. **56,** 986-97 (1923).

(328) Stokes: Ber. **24,** 933-6 (1891).

(329) Stoltzenberg: Chem. Zentr. **100,** 287 (1929).

(330) Taylor and Hildebrand: J. Am. Chem. Soc. **45,** 682-94 (1923).

(331) Thomsen: Pogg. Ann. **139,** 193-224 (1870).

(332) Thomsen: Ber. **16,** 2613-15 (1883).

(333) Thorp: Ber. **9,** 505-10 (1876).

(334) Thorpe: J. Chem. Soc. **37,** 141-225 (1880).

(335) Thorpe: J. Chem. Soc. **37,** 327-94 (1880).

(336) Thorpe: J. Chem. Soc. **41,** 297 (1882).

(337) Tiffeneau: Bull. sci. pharmacol. **29,** 440-2 (1922).

(338) Troost and Hautefeuille: Compt. rend. **70,** 252-5 (1870).

(339) Troost and Hautefeuille: Compt. rend. **73,** 563-71 (1871).

(340) Troost and Hautefeuille: Ann. chim. phys. [5] **7,** 452-76 (1876).

(341) Vaidyanathan: Nature **128,** 189 (1931).

(342) Vigouroux: Compt. rend. **120,** 1161-4 (1895).

(343) Vigouroux: Compt. rend. **141,** 828-30 (1906).

(344) Vigouroux and Arrivaut: Compt. rend. **144,** 485-7 (1907).

(345) von der Pfordten: Ann. **234,** 257-99 (1886).

(346) Vournasos: Z. anorg. Chem. **81,** 364-8 (1913).

(347) Wagner: Ber. **21,** 960-2 (1888).

(348) Walden: Z. anorg. Chem. **29,** 371-95 (1902).

(349) Walker: Ind. Eng. Chem. **17,** 1061-5 (1925).

(350) Walker: Chem. Zentr. **101,** 2475 (1930).

(351) Walter: Monatsh. **64,** 287-8 (1934).

(352) Warren: Chem. News **60,** 158 (1888).

(353) Watts and Bell: J. Chem. Soc. **33,** 442-4 (1878).

(354) Weber: Pogg. Ann. **107,** 375-93 (1859).

(355) Weber: Pogg. Ann. **118,** 471-9 (1863).

(356) Wehrlin and Giraud: Compt. rend. **85,** 288-90 (1877).

(357) Wieland: Ann. **431,** 30-40 (1923).

(358) Williams: J. Chem. Soc. **22,** 304-7 (1869).

(359) Williams: J. Chem. Soc. **49,** 223-33 (1886).

(360) Williams: Bull. soc. chim. [2] **13,** 228 (1870).

(361) Williamson: Proc. Roy. Soc. (London) **7,** 11 (1854).

(362) Williamson: J. Chem. Soc. **10,** 97-102 (1857).

(363) Williamson: Proc. Roy. Soc. (London) **53,** 658 (1861).

(364) Winmill: J. Chem. Soc. **101,** 718-25 (1912).

(365) Wintgen: Ber. **52B,** 724-31 (1919).

(366) Wöhler: Pogg. Ann. **11,** 146-61 (1827).

(367) Wölbling: Z. anorg. Chem. **57,** 281-9 (1908).

(368) Wood: J. Am. Chem. Soc. **59,** 1510-14 (1937).

(369) Yakubovich: J. prakt. Chem. **138,** 159-66 (1933).

(370) Young: J. Chem. Soc. **75,** 172-5 (1899).

(371) Zeide and Gorski: Ber. **62,** 2186-91 (1929).

(372) Zeide, Sherlin, and Bras: J. prakt. Chem. **138,** 225-30 (1933).