CHLOROPICRIN

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INTRODUCTION

In the writing of this monograph an attempt has been made to provide a summary of the work done with chloropicrin (also known as trichloronitromethane and nitrochloroform) and to include all the important work done on this subject up to and including the year 1931. As chloropicrin is used principally as a repellent, fumigant, insecticide, parasiticide, and disinfectant, the literature has been difficult to search, for not infrequently the name does not appear in the title of the paper or in the index of the journal in which the paper is published.

PREPARATION

Chloropicrin was first prepared by Stenhouse (1), who added an aqueous solution of picric acid to an excess of bleaching powder. Considerable study was given to its preparation and the following methods were worked out: by boiling picric acid with potassium chlorate and hydrochloric acid; by boiling picric acid with aqua regia; by bubbling chlorine through a hot aqueous solution of picric acid; by heating potassium picrate with a solution of bleaching powder; by boiling Dammara resin with nitric acid and then treating the resulting product with bleaching powder; by digesting in nitric acid the resinous compound which chlorine formed with usnic acid; by boiling chrysamic acid, styphnic acid, or Erdmann's oxypicric acid with either bleaching powder or potassium chlorate and hydrochloric acid.

Kekulé (2) obtained chloropicrin by the action of alcohol and concentrated nitric acid upon sodium chloride and also (3) by the distillation of solid or liquid chloral with concentrated nitric acid, or with a mixture of nitric and sulfuric acids; or, when a mixture of methyl alcohol and sulfuric acid was distilled with a mixture of sodium nitrate and sodium chloride.

Hofmann (4) prepared chloropicrin by a modification of Stenhouse's (1) original method by making a thick cream with ten parts of fresh bleaching powder, after which it was mixed with a saturated solution of one part of picric acid warmed to 30°C.; as soon as the violent reaction was completed, chloropicrin was distilled over.

Mills (5) prepared chloropicrin by the nitration of chloroform, by heating seven volumes of chloroform with sixteen volumes of nitric acid (containing much nitrogen peroxide) in a sealed tube to 90°–100°C. for 120 hours. It was recommended that the tube be kept at an angle of 30° with the bottom of the bath, as it appeared that a more nearly horizontal position involved the destruction of any nitro compound that may be formed, while an upright position caused the reaction to proceed with excessive slowness.

Green and Rowe (6) found that when sodium hypochlorite was used as an oxidizing agent with dinitroaniline, nitro-*p*-phenylenediamine, nitroacetyl-*p*-phenylenediamine, and the azo compound obtained by combining diazotized nitro-*p*-phenylenediamine with β-naphthol, the ring was ruptured and chloropicrin formed. They also found (7) that when 2,4-dinitronaphthylamine was subjected to hypochlorite oxidation, either in suspension or in alcoholic solution, at the ordinary temperature or when cooled with ice, disruption of the ring resulted, accompanied by a strong odor of chloropicrin, but the compound was not capable of isolation.

Datta and Chatterjee (8) were able to obtain an 85 per cent yield of chloropicrin when acetone was added to ten parts of a slightly warmed mixture of two parts of nitric acid and three parts of hydrochloric acid, warmed for some time on the water bath, and then steam distilled. When allyl alcohol was gradually added to a mixture of the acids (2:3) with occasional warming on the water bath, its transformation was complete. In like manner ether and ethyl alcohol were converted into chloropicrin. And, as the result of extensive investigations, they found (9) that whenever an organic compound broke up destructively under the influence of aqua regia, chloropicrin was invariably produced.

Datta and Fernandes (10) have shown that chloropicrin is formed from hydrocarbons which undergo decomposition by aqua regia (cymene, styrene, diisobutylene, triisobutylene, etc.).

Copisarow (11) in the utilization of trinitrotoluene residues found that chloropicrin could be obtained by the employment of Hofmann's method, and, considering the percentage of nitrogen present, found that the yield compared favorably with that obtained by the degradation of picric acid residues.

Orton and Pope (12) obtained, on May 9, 1918, British patent No. 142,878 for the preparation of chloropicrin by the action of chlorine on picric acid or on other suitable nitro derivatives of a phenol or of a naphthol in the presence of water and a basic material, such as metallic oxides, carbonates, or borates, preferably sodium or potassium hydroxides or carbonates, to dissolve the nitro derivatives and neutralize the acid produced in the reaction. The basic material may be added in successive stages or wholly at the beginning.

King (13) obtained, on January 13, 1920, U. S. patent No. 1,327,714 for a process of producing chloropicrin which consists in forming an admixture of bleaching powder with water, wherein the amount of water is six times the equivalent of lime, and adding thereto a solution of calcium picrate.

Orton and McKie (14) were able to obtain a yield of chloropicrin reaching 200 per cent by passing chlorine into a cooled suspension of sodium picrate in aqueous sodium carbonate. Picric acid was dissolved in a hot solution of four parts of sodium carbonate (17 equivalents) in fifty parts of water. The thin paste was rapidly cooled to below 5°C. (to produce small crystals), and chlorine added slowly or intermittently (too rapid a stream of chlorine not only wastes the gas but in addition produces chlorates). The products are chloropicrin and some nitric acid, together with chloride and some hypochlorite, and chlorate which has arisen from transformation of hypochlorite. For determinations of the hypochlorite, chlorate, and chloride in the aqueous product, it was found that the proportion of the last accords well with the opinion that chloropicrin was formed in a reaction between hypochlorite (hypochlorous acid) and picric acid, thus:

$$C_6H_2(NO_2)_3OH + 11HClO \rightarrow 3CCl_3NO_2 + 2HCl + 3CO_2 + 6H_2O$$

that is,

$$C_6H_2(NO_2)_3OH + 11Cl_2 + 5H_2O \rightarrow 3CCl_3NO_2 + 13HCl + 3CO_2$$

when the maximum yield would be 215 per cent, or,

$$C_6H_2(NO_2)_3OH + 12Cl_2 + 8H_2O \rightarrow 2CCl_3NO_2 + 18HCl + 4CO_2 + HNO_3$$

where the maximum yield would be 143.5 per cent.

Frahm (15) obtained chloropicrin in theoretical amounts by using the less expensive alkali, lime, and carrying out the reaction at 0°C.

Sweeney (16) obtained, on April 18, 1922, U. S. Patent No. 1,413,198 for a process of making chloropicrin by bringing together, under pressure, a suspension of a chlorine-yielding material in water and suspensions of picric acid and lime in water. Oxidation loss and foaming are suppressed.

Chloropicrin has been produced by the action of chlorine upon an aqueous solution of sodium nitranilate and iodine (17); by the action of chlorine on silver fulminate (18); by heating chloroform with acetylnitrate (19); by refluxing dihydro-s-chlorxylol with 30 per cent nitric acid (20); as a by-product when the chloro derivatives of 5-nitrobarbituric acid were formed (21); when 2,4-dichloroacetanilide was warmed with concentrated nitric acid (22); by the action of sodium hypochlorite on nitrophenols (23); by the action of chlorine on 1,3,5-trinitro-2,6-dihydroxybenzene (24); by the oxidation of trichloronitrosomethane (25).

PHYSICAL PROPERTIES

Freshly distilled chloropicrin is a colorless liquid which becomes yellow in diffused light and in sunlight assumes the color of nitrous vapors (26). The boiling point has been determined by several observers. Stenhouse (1) determined it as 120°C. and Hofmann (4) as 112°C.; neither value can be taken as correct, whereas both might be, as the observers did not record the pressure at which their determinations were made. Bertrand (27) gave it as 112.3°C. at 766 mm. and 15°C. at 30.2 mm. Cossa (28) determined its boiling point as 112.8°C. at 743 mm. and Thorpe (29) observed it to be 111.91^{Δ} ($^{\Delta}$air thermometer degree) (corrected) at 751.9 mm., a value which Piutti (26) checked. Blaszkowska-Zakrzewska (30) calculated it as 112.21°C. at 760 mm.

Chloropicrin solidifies in a freezing mixture at −64°C. (31), and at −69.2°C. (corrected) (32). It crystallizes in the shape of long, thin needles possessing a strong double refraction and a parallel extinction, thus belonging to the tetragonal, hexagonal, or orthorhombic systems. No other polymorphic modifications have been observed above −200°C. (33).

The density of chloropicrin at 16°C. was determined as 1.666 (27). The specific gravity at 0°/0° as 1.69247, at 4°/4° as 1.69225 (29), at 20°/4° as 1.6539 (34), at 4°/4° as 1.6855, at 10°/10° as 1.6748, at 15°/15° as 1.6670, at 20°/20° as 1.6594, at 25°/25° as 1.6528 (35).

Chloropicrin is almost insoluble in water. At 0°C. the solubility is 0.2272 g. per 100 cc. of water; at 25°C., 0.1621 g.; at 75°C., 0.1141 g. At 32°C. 100 g. of chloropicrin dissolves 0.1003 g. of water; at 41°C., 0.1243 g.; at 55°C., 0.2265 g. Thus it is shown that chloropicrin is only slightly soluble in water, the solubility decreasing with increase of temperature; water is only slightly soluble in chloropicrin, the solubility increasing with increase in temperature (36). The values obtained are given in tabular and graphical form in tables 1 and 2, also figures 1 and 2.

Chloropicrin dissolves iodine, cinnamic acid, benzoic acid, resins, etc. It is miscible in all proportions with benzene, amyl alcohol, carbon disulfide, and absolute alcohol. At 11°C. one volume of 80.55 per cent alcohol dissolves 3.7 volumes of chloropicrin; one volume of 78 per cent alcohol dissolves 1.3 volumes; one volume of ether dissolves 0.3 volume (28).

A sample of Kahlbaum's chloropicrin dried over calcium chloride and distilled at 111°–111.5°C. under 750.5 mm. showed the following refractive indexes at 22.8°: 1.45740 (Li), 1.45793 (H_α), 1.46075 (Na), 1.46393 (Tl), 1.46785 (H_β), 1.47377 (H_γ) (34).

Chloropicrin dried over phosphorus pentoxide and distilled from anhydrous potassium carbonate at 112°C. showed an average specific magnetic rotation at 12.7°C. of 0.9843, and a molecular rotation of 5.384 (35). For more complete values see table 3.

TABLE 1

Solubility of chloropicrin in water

	TEMPERATURE		
	0°C.	25°C.	75°C.
Grams chlorine in 100 cc. water	0.1472	0.1060	0.0739
	0.1465	0.1048	0.0753
	0.1468	0.1049	0.0695
	—	0.1049	0.0674
	—	0.1042	0.0796
	—	0.1055	0.0768
	—	0.1045	0.0674
Average equivalent of chloropicrin	0.2272	0.1621	0.1141

TABLE 2

Solubility of water in chloropicrin

WATER	CHLOROPICRIN		TEMPERATURE OF MISCIBILITY	WATER PER 100 GRAMS OF CHLOROPICRIN
grams	*cc.*	*grams*	*degrees C.*	*grams*
0.1098	29.3	48.49	55.0	0.2265
0.1098	35.8	59.25	50.8	0.1853
0.1098	40.3	66.70	48.0	0.1647
0.1098	53.4	88.38	41.0	0.1243
0.1098	56.0	92.68	36.0	0.1185
0.1098	66.0	109.25	32.0	0.1003

TABLE 3

Specific magnetic rotation and molecular rotation of chloropicrin

TEMPERATURE	SPECIFIC ROTATION	MOLECULAR ROTATION
degrees C.		
15.6	0.9800	5.376
15.6	0.9804	5.378
15.6	0.9800	5.376
15.6	0.9775	5.363
15.6	0.9810	5.382
9.0	0.9905	5.399
9.0	0.9887	5.389
9.0	0.9905	5.399
9.0	0.9899	5.395
Average...12.7	0.9843	5.384

The specific conductivity of chloropicrin was found to be at least ten times less than that of nitromethane, less than 6×10^{-3} reciprocal ohms (37).

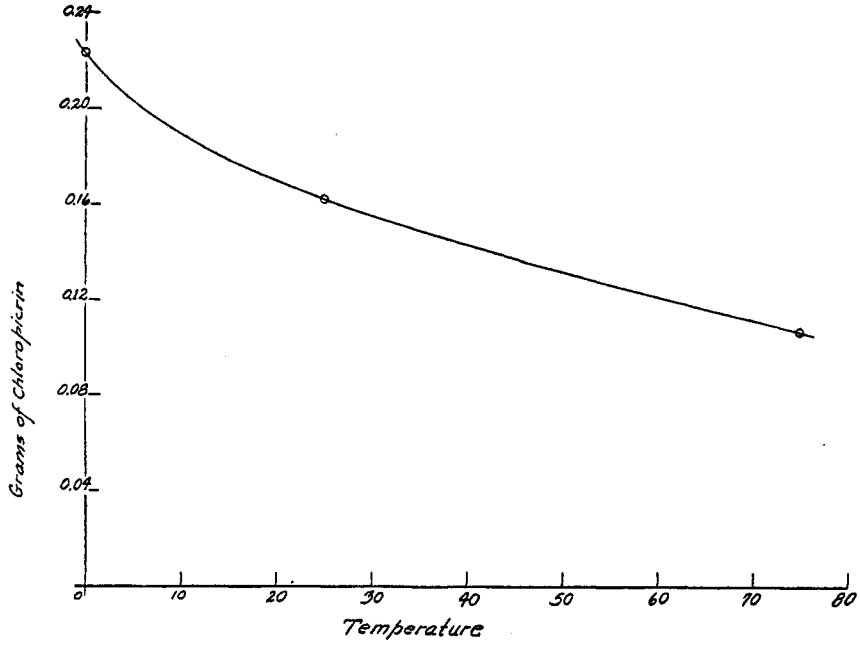


FIG. 1. SOLUBILITY OF CHLOROPICRIN IN 100 GRAMS OF WATER

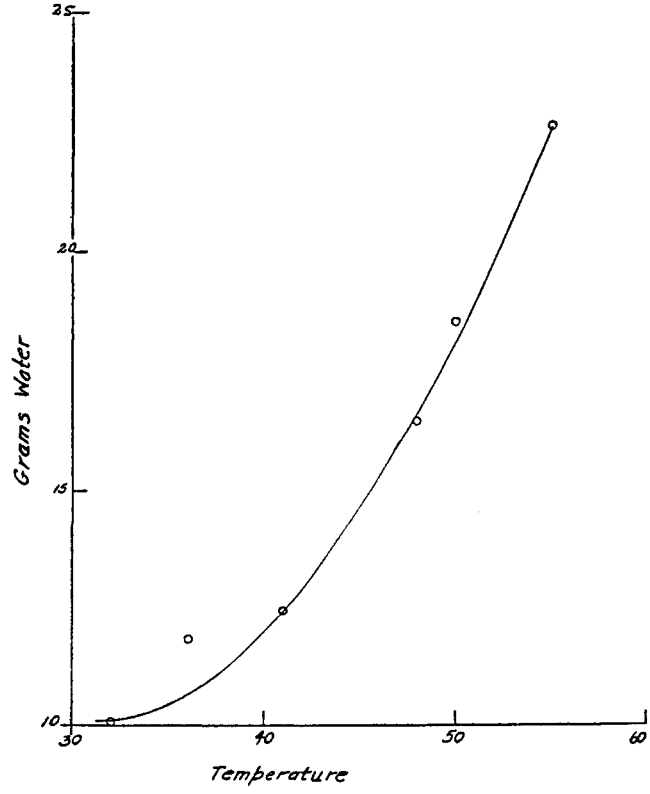


FIG. 2. SOLUBILITY OF WATER IN 100 GRAMS OF CHLOROPICRIN

Cotton and Mouton (38) determined that chloropicrin has a positive magnetic birefringence of 2.0606 at 14.2°C.

The molecular diamagnetism of chloropicrin was shown by Pascal (39) to be 785, which is 115 less than the calculated value. Not only with this compound but in all cases in which two or more halogens are attached to the same carbon atom, quite a discrepancy was found. This was supposed to be due to the formation of double bonds between the halogens as demanded by Thiele's theory.

By means of the formula developed by Kleeman (40)

$$\gamma - t(dy/dt)\ (M_v)^{2/3} = 2.38\ (T_c - 6)$$

where γ = surface tension, t = temperature, and T_c = critical temperature, Bennett and Mitchell (41) calculated the total surface energy for chloropicrin from the data of Schiff (42) and determined it as 1535, the theoretical value being 1558.

The molecular depression of the freezing point of chloropicrin in formic acid varied from 25.7 to 27.4, indicating no dissociation (43). The results on a series of nitrogen derivatives show that the aromatic compounds are all more or less dissociated, while those of the aliphatic series are not. The authors account for this dissociation by supposing the formation of an additive product of the type R—NO(OH) (COOH); one fact in favor of this hypothesis is that solutions of aromatic polynitro derivatives in anhydrous formic acid are colorless even at high concentrations, while with other solvents, whether possessed of dissociating power or not, they form intensely yellow solutions.

The optical absorption of chloropicrin is very similar to that of nitromethane as found by Hantzsch and Voigt (44). Thus it is to be noted that the substitution of chlorine for hydrogen brings about but a very slight effect.

Thorpe (29) calculated the relative volume of chloropicrin. The observations given in table 4 were made with dilatometer in the water bath. Observations made in an oil bath are given in table 5.

These observations may be represented by the formula

$$3378.99 + 3.632970t + 0.00148070t^2 + 0.000026430t^3$$

which gives the numbers in the last columns of tables 4 and 5. Dividing through by the first term and correcting for the expansion of the glass (0.00002553), this expression becomes

$$V = 1 + 0.0011007t + 0.000000465757t^2 + 0.000000007833t^3$$

by the aid of which table 6, showing the relative volume of chloropicrin at every 5° between 0° and 110°, is calculated.

TABLE 4

Expansion of chloropicrin in water bath

Δ*	RELATIVE VOLUME	
	Observed	Calculated
00.00	3378.8	3379.0
10.21	3416.2	3416.3
19.11	3449.4	3449.1
30.66	3492.5	3492.5
40.15	3529.1	3528.9
49.98	3567.5	3567.6
59.67	3606.6	3606.7

* Temperatures expressed in air-thermometer degrees, which are distinguished, in order to prevent confusion, by Bergamm's symbol for fire or heat.

TABLE 5

Expansion of chloropicrin in oil bath

$T°$	$t°$	T	V	E	VOLUME	
					Observed	Calculated
70.50	23.5	70.43	3638.7	247.0	3651.7	3651.4
80.31	25.4	80.38	3676.1	284.7	3694.3	3694.3
89.25	28.3	89.46	3711.7	320.3	3734.7	3734.8
102.81	30.4	103.32	3766.3	374.9	3799.4	3799.3
107.84	31.8	108.44	3786.8	395.4	3823.9	3824.1

TABLE 6

Relative volume of chloropicrin between 0^{Δ} and 110^{Δ}

Δ	VOLUME	DIFFERENCE	Δ	VOLUME	DIFFERENCE	Δ	VOLUME	DIFFERENCE
0	100000	—	40	104528	585	80	109505	657
5	100552	552	45	105119	591	85	110174	669
10	101016	554	50	105718	599	90	110855	681
15	101664	558	55	106325	607	95	111549	694
20	102226	562	60	106941	616	100.00	112256	707
25	102793	567	65	107567	626	105.00	112978	722
30	103365	572	70	108202	635	110.00	113714	736
35	103943	578	75	108848	646	111.91	113999	—

By combination with van't Hoff's equation for E, the molecular rise of boiling point, the equation

$$E = 0.001115T_c^2/a_c^2$$

was derived, and using the data of Schiff (42). Walden (45) calculated the

specific cohesion of chloropicrin at its boiling point as 2.82. From the equation

$$\lambda_\sigma = 46a_\sigma/\log T_\sigma$$

the latent heat of vaporization was calculated as 50.2 calories per gram.

Aston and Ramsay (46), from the molecular surface energy and its variation with temperature, found chloropicrin to have a normal molecular weight.

Baxter, Bezzenberger, and Wilson (47) determined the vapor pressure of chloropicrin 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 chloropicrin by passing 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 22.41 liters. The per cent of vapor by volume multiplied by the interior pressure, as determined by the barometric reading and an open-arm water manometer attached to the aspirator, gives the vapor pressure. The control of temperature in the thermostat was within 0.1°C. except when a freezing mixture was employed, where the uncertainty may have been as large as 1°C. at −18°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

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

Satisfactory values of A and B were computed.

Vapor pressures calculated by means of these equations agree with the observed values within the experimental error. For a higher degree of accuracy the equations were not adequate, however, and can not be trusted for extrapolation over any considerable range.

The original chloropicrin was distilled in a partial vacuum in two portions. The first was used at 35°, 25°, 15°, and 0°C.; the second at the other temperatures.

$$\log \text{ vapor pressure} = 8.2424 - 2045.1/273 + t$$

The data in table 7 furnish evidence from which the heats of vaporization may be computed. Using the Clausius-Clapeyron equation

$$L = T\, \mathrm{d}p/\mathrm{d}t\, (V_{\text{gas}} - V_{\text{liquid–solid}})$$

and values for the vapor pressures calculated from the logarithmic vapor pressure equations, the results are expressed in kilogram-calories per gram molecule. The heat of vaporization is 6.77 at 35°C. and 7.10 at 0°C.

The vapor tension of chloropicrin was determined (30) from 98°C. to 105°C. in Swietoslawski's ebullioscopic thermostat by the "air current" method. The apparatus consists of a 500- to 600-cc. flask connected by a narrow tube with the thermostat proper, a cylinder of 55 mm. diameter which carries a thermometer, a siphon fused into the bulb of the flask and a reflux condenser; the latter is connected with the pressure regulating system. The apparatus in which the air current is saturated with the vapors was constructed by Wojnicz-Sianozecki and resembles Gahl's wash bottle (48). The velocity of the air current was 300 cc. per minute. The

TABLE 7

Vapor pressure of chloropicrin

TEMPERATURE	VOLUME OF AIR AT 0°C. AND 760 MM.	LOSS IN WEIGHT OF SATURATION TUBE	INTERIOR PRESSURE	VAPOR PRESSURE (Observed)	VAPOR PRESSURE (Calculated)	DIFFERENCE (Calcd.–observed)
°C.	cc.	grams	mm.	mm.	mm.	mm.
35	2185	0.9222	736.9	40.14	40.04	−0.10
30	2434	0.7571	764.5	31.10	31.10	0.00
25	2670	0.6428	749.5	23.81	23.97	0.16
20	2184	0.3963	759.1	18.31	18.30	−0.01
15	2972	0.4053	756.6	13.82	13.85	0.03
10	2745	0.2790	758.2	10.37	10.37	0.00
0	2559	0.1468	735.3	5.71	5.64	−0.07
−18	3299	0.0611	754.1	1.90	1.67	−0.23
−19	3400	0.0566	751.5	1.70	1.55	−0.15
−20	3125	0.0459	751.8	1.50	1.44	−0.06

mean error was 0.6°–0.8°C. The values obtained were 502.1 at 98°C., 532 at 100°C., 564.4 at 102°C., 567.6 at 103°C., 583 at 104°C., and 597 at 105°C.

The "immersed bulb" method (49) permits determinations of vapor tension with very small amounts of material (0.03 to 0.05 g.) and with greater accuracy than by the "air-current" method. The bulb was placed in the ebullioscopic thermostat for the determination of the vapor pressure of chloropicrin from 97°C. to 105°C. The following values were obtained: 491.4 at 98°C., 524.3 at 100°C., 558.2 at 102°C., 557.9 at 103°C., 595.2 at 104°C., and 612.8 at 105°C. These results differ considerably from those obtained by the "air-current" method and may be considered more trustworthy, because of the experimental errors inherent in the latter (too high velocity of the air current and carrying over of liquid drops) and because

Avogadro's law, which underlies the calculations of vapor tension by the dynamic method, probably does not obtain for saturated vapors. The curve

$$\ln p - 1/T$$

is a straight line, or

$$\ln p = A - (B/T)$$

where $A = 7.8704$ and $B = 1921.4$. Baxter, Bezzenburgh, and Wilson (47) however, determined $A = 8.2424$ and $B = 2045.1$, and stated that the

TABLE 8

Freezing points of binary mixtures of chloropicrin and nitrogen peroxide

CHLOROPICRIN	NITROGEN PEROXIDE	TEMPERATURE AT WHICH MELTING	
		Started	Finished
per cent	*per cent*	*degrees C.*	*degrees C.*
100	0	−64.0	−64.0
95	5	−72.0	−79.5
92	8	−79.5	−79.5
89	11	−67.5	−79.5
70	30	−42.5	−79.5
50	50	−27.5	−67.5
30	70	−18.0	−30.0
20	80	−15.0	−23.5
10	90	−12.0	−16.0
0	100	−10.2	−10.2

equations were not adequate over any considerable range. Hertz's equation (50)

$$\ln p = \alpha - (\beta/T) - (\gamma \ln T)$$

where $\alpha = 18.3014$, $\beta = 2485.5$, and $\gamma = 3.468$, covers the entire temperature interval from 0°C. to the boiling point, and the calculated results agree well with the experimental ones.

Pascal (51) determined the freezing point of a series of binary mixtures of chloropicrin and nitrogen peroxide as shown in table 8.

At 32°C. and under a pressure of one atmosphere, 3.4 pounds of chloropicrin can exist in the vapor phase in a 1000 cu. ft. chamber (52).

Flury (53) determined the volatility of chloropicrin as 175,000 cu. mm. per cubic meter.

Lecat (54) formed azeotropic mixtures with chloropicrin (b.p., 111.85°C.) and a number of compounds (see table 9). Nonazeotropes formed with toluene and acetal.

Allyl alcohol, dimethylethylcarbinol, normal butanol, and isobutylcarbinol form positive azeotropes with chloropicrin; methyl alcohol and normal hexanol form nonazeotropic systems with chloropicrin (55).

Chloropicrin and sixty-two other halogen-containing organic compounds were used by Tronov (56) in making a study of the activity of the halogens. A small quantity of a halogen compound was taken to react with about one mole of pyridine or piperidine in a sealed tube and the product of the reaction titrated with silver nitrate. As the result of these investigations it was found that the mobility diminishes from iodine to bromine and chlorine. This difference was considerable with aliphatic but less with aromatic compounds. The mobility of a halogen decreases with the increase in length of the hydrocarbon chain and the proximity of a side chain. A primary is more mobile than a secondary halogen. The proximity of a double bond decreases the mobility of a halogen compound. Oxygen increases the mobility of C:O > oxide O > OH. The influence on

TABLE 9

Azeotropic mixtures of chloropicrin with other compounds

CHLOROPICRIN	COMPOUND	BOILING POINT OF AZEOTROPIC MIXTURE
per cent		*degrees C.*
35.0	Ethyl alcohol (b.p., 78.3°C.)	77.4
33.5	Isopropyl alcohol (b.p., 82.45°C.)	82.0
58.5	Propyl alcohol (b.p., 97.2°C.)	94.0
67.5	Isobutyl alcohol (b.p., 107.85°C.)	102.05
29.0	Methylcyclohexane (b.p., 101.1°C.)	100.75

the mobility of a halogen atom of other halogen atoms in the molecule is more complicated. But even in this case it has been noticed that the splitting takes place more readily the more positive the radical is.

Harned (57), making measurements of the velocity of adsorption of chloropicrin at 20°C. by wood charcoal (14 to 16 mesh) which contains 6 per cent non-volatile material, showed that there is sometimes an initial lag in adsorption, and that in all cases discordant and unreproducible results are obtained except when the reaction is proceeding at the maximum velocity obtainable under a given set of temperature and pressure conditions. At the maximum velocity, adsorption occurs in accordance with the equation

$$\log K = \log A - B/t$$

where K is the weight of the gas in grams per gram of charcoal adsorbed in time t, and A and B are constants. The velocity constant is given by the expression

$$m = (1/t) \log [A/(A - K)]$$

The results obtained with chloropicrin indicate that a tenfold decrease in pressure has been found to cause a forty-twofold decrease in m; at higher pressures the capacity of charcoal varies but little with pressure. Thus, the capacity per gram of charcoal amounts to 0.2800 g. at a pressure of approximately 5×10^3 bars and to 0.3100 g. at 5×10^4 bars. The data agrees qualitatively with the one-layer theory regarding the capacity as developed by Langmuir (58). (See table 10 and figure 3.)

TABLE 10

Adsorption of chloropicrin by charcoal

p = 5.90 mm.; t = time of exposure in seconds; K = weight of gas adsorbed per gram of charcoal in time t

I		II		III	
t	K	t	K	t	K
1.6	0.0030	1.6	0.0056	2.2	0.0091
3.2	0.0070	2.8	0.0082	5.4	0.0221
5.7	0.0116	5.1	0.0159	8.6	0.0374
9.1	0.0241	7.4	0.0234	13.8	0.0568
14.4	0.0418	9.7	0.0305	24.3	0.0753
25.1	0.0636	15.0	0.0479	6600.0	0.1854
463.0	0.1578	25.4	0.0728		
		503.0	0.1406		

I. Weight of charcoal = 0.8420 g. Heated to 350°C. for 2 hours in a high vacuum, cooled and maintained at 20° ± 1°C. The tube containing chloropicrin was kept in ice water. By keeping the liquid reservoir at a temperature lower than the charcoal, distillation was avoided.

II. Same charcoal, same weight as in I. No air or moisture was permitted to come into contact with the charcoal between measurements I and II. Reheated to 350°C. for 2.5 hours in a high vacuum. Gain in weight of charcoal equalled 10 mg. Same temperature conditions during velocity measurements as in I.

III. Same charcoal. Reheated to 350°C. for 7 hours in a high vacuum. No foreign gas admitted. Gain in weight of charcoal equalled 1.5 mg. Same temperature conditions as in I and II.

Adsorption decreases with rising temperature (59). This temperature effect is slight at higher pressures, but much more pronounced at lower pressures. The variation of adsorption with temperature also increases as the boiling point of the gas is approached.

Moisture is more highly adsorbed at ordinary temperature by charcoal than any other of the normal constituents of the air. On the other hand, it is much less adsorbed than such toxic gases as chloropicrin for instance. Thus an active charcoal will adsorb and retain 25 per cent of its own weight of chloropicrin at 20°C. and will adsorb an approximately equal amount of

water if it is exposed to saturated water vapor at the same temperature, but it holds this water very feebly, losing all but 1 or 2 per cent of it when it is exposed to dry air for some time. Figure 4 a shows the effect of humidity on the adsorption of chloropicrin by a rather poor sample of charcoal at 20°C.

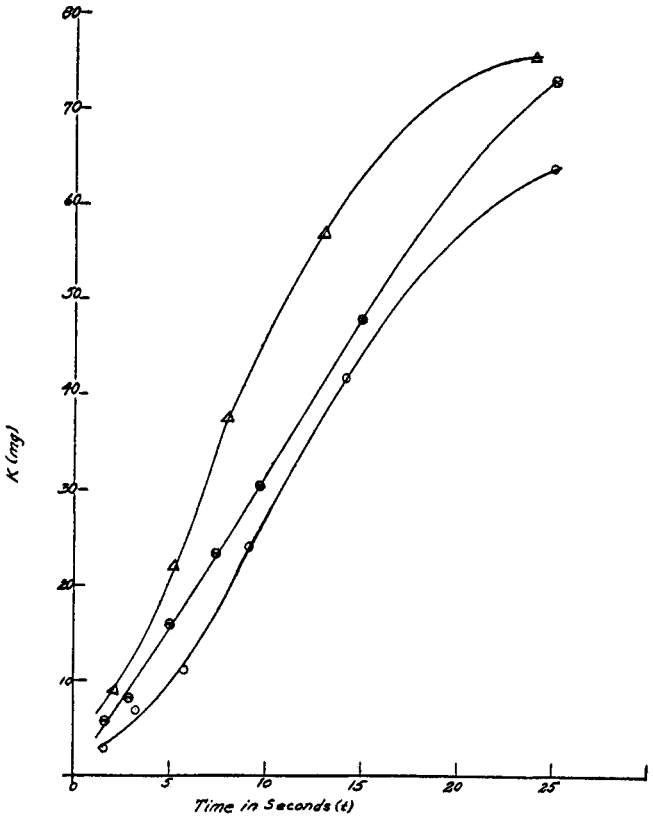


FIG. 3. ABSORPTION OF CHLOROPICRIN BY CHARCOAL

p = 5.90 mm.; t = time of exposure in seconds; K = weight of gas absorbed per gram of charcoal in time t.

The dynamic activity of an adsorbent layer is characterized by the time of protective action, which is defined as "the time from the beginning of flow of gas to the moment when the gas appears on the exit side of the adsorbing layer." Dynamic activity of charcoal is usually detected by passing a stream of air containing a small amount of chloropicrin through the charcoal. The method of Dubin, Solov'ev, and Shilin (60) of deter-

mining the "moment of jump" of the stream of gas after passing through charcoal is by allowing the issuing gas to pass through a tube bent at a right angle at the end and placed just above, but not touching, the surface

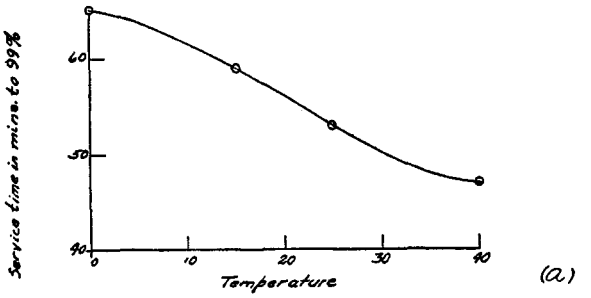


FIG. 4a. EFFECT OF TEMPERATURE ON SERVICE TIME TO 99 PER CENT EFFICIENCY OF CHLOROPICRIN AT 0.7 PER CENT CONCENTRATION OF DRY AIR

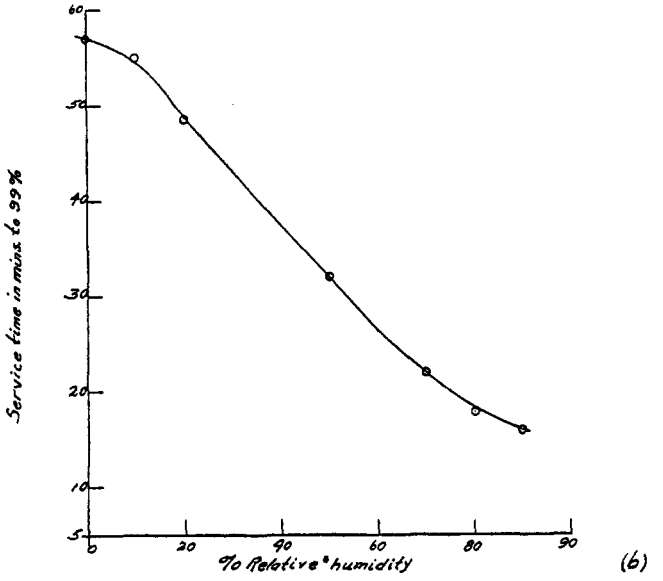


FIG. 4b. EFFECT OF HUMIDITY OF GAS-AIR ON SERVICE TIME OF EQUILIBRATED CHARCOAL AGAINST CHLOROPICRIN CONCENTRATION
Concentration, 0.7 per cent; depth of layer, 10 cm.

of a starch–iodide solution. A piece of filter paper dipping into the solution is placed in front of the tube so that when chlorine is present in the issuing air stream it produces the characteristic mark on the wet filter paper. This method is described as exceedingly delicate.

Chloropicrin is best adsorbed by dyed new wool and dyed used silk, while linen is the poorest adsorbent (61).

Results of experiments (62) have left no doubt that small concentrations of chloropicrin are adsorbed very quickly when exposed to comparatively large rubber or rubberized surfaces. A strip of sheet rubber, 1 in. × 8 in., was suspended in an adsorption bulb, a known amount of gas was then put into the bulb, and the gas allowed to remain in contact with the rubber for time intervals ranging from 15 minutes to 16 hours. At the end of the selected interval the residual gas was drawn through the adsorbing solution and analyzed (see figure 5).

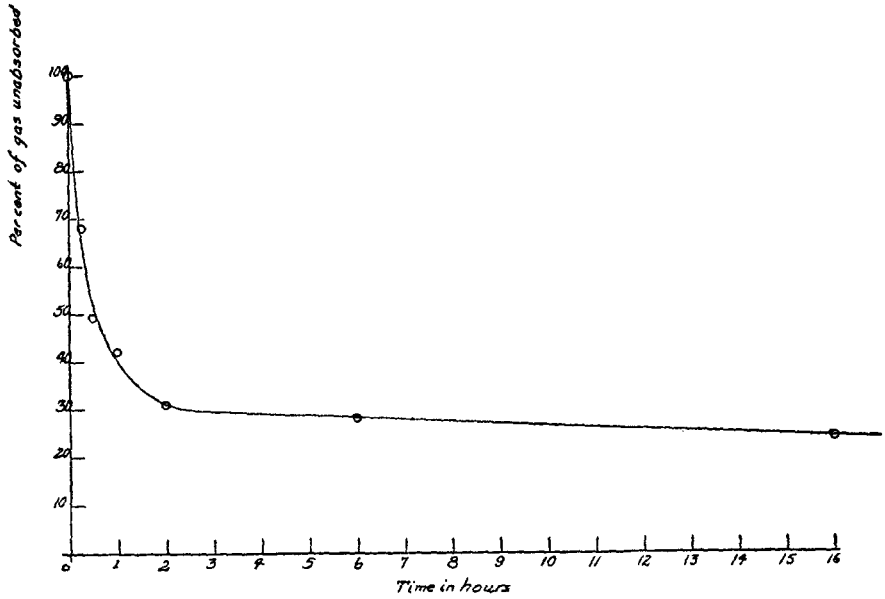


FIG. 5. ABSORPTIVE POWER OF RUBBER FOR CHLOROPICRIN

Volume of bulb, 1000 cc.; area of rubber, 8 square inches; concentration of chloropicrin, 650 p.p.m. initial.

Bouyoucos (63) determined the heat of adsorption of chloropicrin by using active charcoal which had been de-ashed and outgassed at 900°C. and obtained the results as shown in table 11.

Blaszkowska-Zakrzewska (64) determined that at about 140°C. a drop of chloropicrin evaporated on an aluminum bronze surface in minimum time. This is characteristic and depends on the nature of the surface. The evaporation begins by increasing with the rise in temperature, reaches a definite maximum, and afterwards decreases. This decrease of the rate of evaporation with further rise of temperature is produced by the so-called

spheroidal state of the liquid, known as Leidenfrost's effect. The spheroidal state evidently impedes evaporation, since in this state liquid no longer wets a given surface.

CHEMICAL PROPERTIES

Auwers and Harres (65), using the spectrochemical method, confirmed the usually accepted structure of a normal nitro compound for chloropicrin.

At its boiling point chloropicrin slowly decomposes into carbonyl chloride and nitrosyl chloride.

$$CCl_3NO_2 \rightarrow COCl + NOCl$$

It was determined by Gardner and Fox (66) that 200 cc. of chloropicrin, held at its boiling point, decomposes at the rate of 2 cc. per day.

TABLE 11

Heat of adsorption of chloropicrin at 0°C.

A	Q	$\Delta Q/\Delta A$
cc.	*joules*	
0.307	20.84	67.9
0.672	42.48	59.3
1.012	59.89	51.2

A = total amount of gas adsorbed per gram of adsorbent reduced to standard conditions.

B = total amount of heat (expressed in millijoules) evaporated by the adsorption of A.

At 100°C. chloropicrin is decomposed rapidly by sulfuric acid containing 20 per cent of the anhydride, into phosgene and nitrosyl chloride. A 73 per cent yield may be obtained in 35 minutes (67).

Solutions of chloropicrin in ethyl alcohol, methyl alcohol, benzene, turpentine, acetic acid, etc., remain unchanged in the dark, but when exposed to light all except those in the alcohols become colored. The solutions in alcohols, after one day, separate into two layers, and white crystals of ammonium chloride separate at the bottom. Acetone solutions are somewhat colored and do not separate in two layers, but deposit ammonium chloride. Evidently the alcohols reduce the NO_2 to NH_2 and then to NH_3. Reductions by alcohol in light were observed by Ciamician and Silber (68) and others, but this instance is striking because the NH_2 is reduced only in the light. The alcohol or acetone solutions may be boiled in the dark and remained unchanged (26).

Piutti (69) further showed that when certain compounds are present with chloropicrin, decomposition of the latter by light is accompanied by

oxidation, chlorination, or nitration of the other compound, depending on its nature. Solutions of chloropicrin in acetic acid (m.p., 16.5°C.) turned yellowish brown and separated into two layers in one day; in the lower layer crystals of formic acid separated in one month, and increased in amount for six months. The lower layer, on distillation from 90–115°C., yielded unaltered chloropicrin. Aqueous extracts of the distillate and of the residue contained chlorine, hydrochloric acid, nitrous acid, and unaltered acetic acid. The upper layer, distilled at 128°C., yielded fractions containing these same compounds, but when distilled in vacuum for 40 minutes at approximately 84°C., monochloroacetic acid was recovered. Equal parts of diethyl succinate and chloropicrin after 4 days exposure to light precipitated a crystalline mixture of succinic acid with a small amount of oxalic acid which increased in amount for one month. With equal volumes of methyl salicylate and chloropicrin a mixture of 1,2,3-methylchlorosalicylate (m.p., 48°C.), oxalic acid, ammonium tetroxalate, and a brown resin first appeared in five days and increased in amount for one year. Equal volumes of toluene and chloropicrin first turned yellow, then brown; after two months oily drops appeared, and after five months both large white and minute colorless crystals. Fifty grams of toluene and 50 g. of chloropicrin gave, after seven months, 13.2 g. of benzoic acid, some oxalic acid, and a brown liquid. The latter separated into two layers, containing hydrochloric acid and *o*-nitrotoluene. A mixture of naphthalene and chloropicrin turned brown after four days, and became lighter in twenty days with the appearance of crystals. The latter increased for three and one-half months and yielded 4.34 g. of benzoic acid and 3.79 g. of phthalic acid from 50 g. of naphthalene and chloropicrin.

Chloropicrin decomposes under the action of ultra-violet light. The products are at first nitrosyl chloride and phosgene, but the latter splits into carbon monoxide and chlorine (70).

Kling and Florentin (71), basing their work on that of Gardner and Fox (66), showed that chloropicrin decomposes slowly into nitrosyl chloride and phosgene, a reaction permitting the supposition that this body is susceptible of taking the tautomeric form $O{:}N{-}\underset{\displaystyle Cl}{O}{:}C{:}Cl_2$.

When hydrogen chloride is passed through chloropicrin at 100°C. and the mixed vapor passed through a tube filled with pumice and heated to 400°C., the bulk of the chloropicrin is decomposed into phosgene, nitrosyl chloride, and nitric oxide, but a small portion is converted into hexachloroethane (72).

On heating chloropicrin to 100°C., in contact with copper, brass, tin, cadmium, zinc, aluminum, lead, and iron the decomposition is slight, but at the boiling point of chloropicrin the rate of decomposition is increased

tenfold (73). The rate of decomposition is practically proportional to time. The catalytic effect of iron and lead is smallest while that of brass is greatest.

The action of chloropicrin on smooth metallic surfaces at room temperature is very slight; the activity is increased if the atmosphere is humid, yet the metals are not completely destroyed. Alekseevskii and Alekseev (74) explain this by supposing that the metals gradually acquire passivity.

When chloropicrin is heated to 100°C. in a closed vessel with fused potassium acetate and alcohol, decomposition takes place with great ease (75).

$$CCl_3NO_2 + 9CH_3COOK + 3C_2H_5OH \rightarrow 3KCl + KNO_2 + K_2CO_3 + 3CH_3COOC_2H_5 + 3(CH_3COO)_2KH$$

On heating a mixture of one part of chloropicrin with three parts of aniline to 145°C. a violent reaction takes place and carbotriphenyltriamine is formed.

By the action of metallic sodium on a solution of chloropicrin in absolute alcohol, ethyl orthocarbonate is obtained (76).

$$CCl_3NO_2 + 4C_2H_5ONa \rightarrow 3NaCl + NaNO_2 + C(C_2H_5O)_4$$

Chloropicrin and sodium methylate react vigorously to form tetramethyl orthocarbonate (77).

By heating chloropicrin with a strong alcoholic solution of ammonia in an autoclave at 100°C. for several hours, guanidine is obtained (78).

$$CCl_3NO_2 + 3NH_3 \rightarrow H{-}N{:}(CNH_2)_2 + 3HCl + HNO_2$$

When chloropicrin is heated in a sealed tube with fuming hydriodic acid, the following reaction takes place (79).

$$CCl_3NO_2 + 6HI \rightarrow NH_3 + CO_2 + 3HCl + 6I$$

By the action of potassium cyanide upon chloropicrin in dilute alcohol, dinitrilechloronitromalonate is formed (80). When chloropicrin is digested with a concentrated, warm solution of potassium bisulfite, it is largely converted into potassium nitroformicdisulfonate (81). In the presence of anhydrous aluminum chloride, chloropicrin and benzene react to form triphenylmethane and triphenylcarbinol (82). By the action of zinc methyl upon chloropicrin, tertiary nitrobutane is obtained; by the action of zinc ethyl upon chloropicrin, nitroheptane, secondary nitropentane, and primary nitropropane are formed (83).

The products of the reduction of chloropicrin seem to vary with the nature of the reducing agent. With stannous chloride and hydrochloric

acid (84), trichloronitromethane is produced which, in turn, decomposes into cyanogen chloride and hydrogen chloride. The occasional formation of traces of ammonia was noticed but, as a rule, after removing the tin by means of hydrogen sulfide, the product was found to be free from ammonium chloride and the hydrochlorides of hydroxylamine and methylamine. Iron filings and acetic acid (85) or tin and hydrochloric acid (86) give rise to monomethylamine.

$$CCl_3NO_2 + 12H \rightarrow CH_3NH_2 + 3HCl + 2H_2O$$

Owing to the importance of methylamine in synthetic organic chemistry and to the fact that chloropicrin was easily obtained in large quantity from gas shells, it appeared to Frankland, Challenger, and Nicholls (87) desirable to investigate more closely its reduction. By employing fine iron filings and hydrochloric acid it was found that the composition of the reduction product depended upon the conditions of the experiment. The use of iron and hydrochloric acid in the theoretical quantities (six atomic proportions of iron and nine molecular proportions of acid to one of chloropicrin) in such a way as to prevent the formation of ferrous or ferric hydroxides gave a product rich in ammonium chloride. If chloropicrin is shaken with iron filings and water, the mixture becomes extremely hot and a vigorous reaction sets in, which, however, gradually slackens if no acid is added. By adopting the method employed in the reduction of aromatic nitro compounds or of nitromethane and nitroethane (88), the reaction proceeds satisfactorily in the presence of only about one-fortieth of the theoretical amount of hydrochloric acid, and a practically theoretical yield of methylamine hydrochloride is obtained.

It would thus appear that the formation of methylamine by reduction is due to reaction of chloropicrin as such, whereas ammonia is to be regarded as derived from the decomposition products (89).

Henderson and Macbeth (90) demonstrated that titanous chloride reduced the nitro group in chloropicrin and left the halogen unattacked.

When chloropicrin is condensed with ethyl sodiomalonate and with ethyl sodiocyanoacetate, the products formed are ethyl ethanetetracarboxylate or ethyl α,α'-dicyanosuccinate, respectively (91).

At ordinary temperatures calcium iodide and chloropicrin do not react, but at 45°C. a reaction begins with the separation of iodine (92). Chloropicrin causes copper to dissolve rapidly in concentrated ammonia water (93).

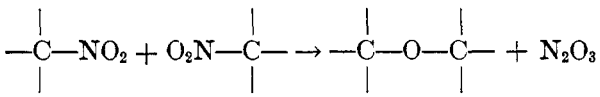
Chloropicrin is attacked but slowly by alkaline solutions of hydrazine and only one chlorine atom is removed. It was found that the quality of the chloropicrin had a great effect on the reaction, as a sample which had been freshly distilled under reduced pressure gave qualitative results (94).

$$2CCl_3NO_2 + N_2H_4 + 4KOH \rightarrow 2CCl_2KNO_2 + 2KCl + N_2 + 4H_2O$$

Chloropicrin reacts readily with mercaptides: at ordinary temperatures the reaction is

$$3RSH + NO_2CCl_3 \rightarrow (RS)_3CNO_2 + 3HCl$$

while at higher temperatures the reaction proceeds further.



It has been recommended that chloropicrin be used as a reagent for the diagnosis of mercaptans and potential mercaptans (95).

Nekrassow and Melnikow (96) have shown that chloropicrin acts as an oxidizing agent with the simplest mercaptans. Ethyl mercaptan, thiophenol, and thio-*p*-cresol give with chloropicrin products which the molecular weight determinations confirmed as the corresponding disulfides, rather than as condensation products of high molecular weight. With ethyl mercaptan there is obtained, instead of Ray's product melting at 123°C., a substance melting at 151.5°C.; this is apparently diethylenetetrasulfide or some oxidation product of $(CH_2SH)_2$. With mercaptides there is always a considerable evolution of gas consisting, along with carbon dioxide, chiefly of nitrogen with not inconsiderable and approximately equal amounts of carbon monoxide and nitric oxide. The main reaction is represented by the equation,

$$2(RS)_3CNO_2 \rightarrow 3R_2S_2 + 2CO_2 + N_2$$

and is accompanied to a smaller extent by the reaction

$$2(RS)_3CNO_2 \rightarrow 3R_2S_2 + 2CO + 2NO$$

The reaction with the free mercaptans is very slow, but the potassium mercaptides react immediately even in the cold, and as the resulting disulfides are practically insoluble in water, the reaction can be used to detect traces of chloropicrin in aqueous solutions. Phenyl mercaptan is especially well adapted for this purpose; with 0.01 mg. of chloropicrin in 1 cc. of water, made faintly alkaline, a few drops of alcoholic thiophenol produce an opalescence and with higher concentrations a precipitate.

The interaction of chloropicrin and phenol in the presence of potassium hydroxide results in the elimination of the nitro group, which effects oxidation and is itself reduced to ammonia. The principal products are *o*- and *p*-salicylic aldehyde, and the corresponding acids. Large quantities of *p*-rosolic acid are also formed, probably by condensation of the phenol with the salicylic aldehyde (97).

The reaction of chloropicrin with phenylmagnesium bromide takes place as follows and is accompanied by a brilliant green fluorescence (98).

$$3C_6H_5MgBr + Cl_3CNO_2 \rightarrow (C_6H_5)_3CNO_2 + 3Mg\begin{matrix}Cl\\ \diagup\\ \diagdown\\ Br\end{matrix}$$

The action of methylmagnesium iodide on chloropicrin, and on other nitro compounds, gave more gas than the equivalent of one active hydrogen, the amount of which varied with the reaction time. Gilman and Fothergill (99) attributed the gases formed to the presence of the nitro group and not to active hydrogen, since nitro compounds containing no hydrogen (as chloropicrin) still yielded them.

Alkali polysulfide solutions destroy the odor of chloropicrin. A yellow color is obtained when a drop of chloropicrin is boiled with alcoholic potassium hydroxide and a small quantity of thymol. The substitution of resorcinol for thymol produced a red color. The addition of sulfuric acid to the thymol mixture produced a reddish violet color, and the whole mixture on dilution with acetic acid exhibited an absorption band in the green portion of the spectrum. Chloropicrin forms carbylamine. Chloropicrin when boiled with potassium hydroxide solution gives, after cooling, reactions characteristic of nitrous acid (100).

When iodine and potassium iodide dissolved in methyl alcohol are poured together and allowed to stand in contact with chloropicrin, the following reaction takes place (101):

$$CCl_3NO_2 + 4KI \rightarrow CI_4 + 3KCl + KNO_2$$

With one, two, or three moles of potassium iodide to one mole of chloropicrin there is obtained carbon tetraiodide but no iodine-substituted chloropicrin. Analogous results are obtained in ethyl alcohol and benzene; the reaction, however, proceeds with a greater speed without the use of solvents.

Elbs and Wittich (102) prepared ditolylmethane and tritolylmethane by distilling a mixture of chloropicrin and toluene, diluted with an equal volume of carbon bisulfide, with zinc dust.

DeForcrand (103) prepared from chloropicrin a compound having the formula $CCl_3NO_2 + 2H_2S + 23H_2O$.

Gardner and Williams (104) obtained, on March 13, 1922, British patent No. 198,462 for the employment of chloropicrin as a nitro oxidizing agent in place of nitrobenzene in the synthesis of quinoline and its derivatives which are, in turn, used in the preparation of Alizarin Blue and other dyes.

Trumbull and Evans (105) obtained, on March 1, 1922, U. S. patent No.

1,402,195 for a process of making crystal violet in which chloropicrin and dimethylaniline are used.

When 10 g. of chloropicrin and 30 g. of dimethylpyridine are mixed in a hermetically sealed flask and left standing at room temperature for eight days, the nitro group of chloropicrin is first split off and the nitration of dimethylpyridine takes place, as indicated by the appearance of a cherry red coloration after twenty-four hours. The chlorine is split off and the first signs of formation of methyl violet appear after three to four days. The liquid thickens, darkens, and finally crystallizes, while the odor of chloropicrin disappears (106).

Backer and Klaassens (107) prepared the anhydrous dipotassium salt of nitromethanedisulfonic acid by gradually adding 82 g. of chloropicrin to 450 g. of potassium sulfite in 900 cc. of water, heated to 75°C., and keeping the temperature at 80°C.

Chloropicrin slowly oxidizes potassium iodide to iodine and hemoglobin to methemoglobin (108).

Chloropicrin gives with amines and many hydrocarbons colored addition compounds (109). The results indicate that the colored compounds result from the interaction of subsidiary valencies associated with the NO_2 group on the one hand and with the C:C or the N atom on the other. In general, it appears that the production of color, in the case of nitro compounds, is always a consequence of the saturation of the subsidiary valencies of the NO_2 group.

Cuprous chloride in concentrated ammonium hydroxide colors chloropicrin first green, then dark blue in two to three minutes, and finally results as a yellowish precipitate (110).

DETECTION

An aqueous solution of chloropicrin reduced with metallic calcium gives some nitrous acid, shown by the red precipitate with β-naphthylamine and sulfuric acid. The reaction is sensitive to 0.002 mg. per liter but not suitable for a quantitative determination (111).

Chloropicrin is easily detected (qualitatively) with a test paper which has been previously soaked in a dilute solution of dimethylaniline in benzene. In the presence of chloropicrin there is a momentary fading, according to the concentration, from bright yellow to dark brown.

For a quantitative determination the chloropicrin–air mixture is drawn through glacial acetic acid in a spiral wash flask and reduced by nascent hydrogen generated from iron. After filtering, it is strongly acidified with nitric acid and precipitated with silver nitrate and the chlorine determined according to Volhard. A second method is accomplished by the thermal decomposition of the air drawn through a glass tube filled with potassium

carbonate and heated to 300–500°C. The chlorine is determined as before (112).

PHYSIOLOGICAL ACTION

Flury (113) determined man's toleration limit for chloropicrin to be 60 cu. mm. per cubic meter of air and Hanslian (114) states that 2400 mg. of chloropicrin per cubic meter of air will kill a man if breathed for 1 minute.

Exposure to chloropicrin causes lachrymation, coughing, nausea, and vomiting, and, in large quantity, it may cause unconsciousness. Secondary effects are bronchitis, shortness of breath, a weak irregular heart beat, and gastritis; it may also lead to acute nephritis. The detrimental influence of this agent is confined to the respiratory tract, and all the other effects must be regarded as secondary; the epithelium of the respiratory tract is injured, the medium and small bronchi being most affected. There is a uniform widespread damage of the alveolar walls, which, however, is not severe enough to lead to necrosis. The alveoli are apparently nowhere protected by constriction of the bronchi. Overwhelming edema of the lungs rapidly follows exposure to the lethal concentration of the gas. In extreme cases practically every alveolus is filled with fluid. The direct cause of death is the extreme concentration of the blood which is brought about by edema (115).

Liquid chloropicrin has a corrosive action on the skin, and scratches and abrasions exposed to chloropicrin fumes invariably become septic. Abscess formation may result (116).

The most efficacious method of treatment in chloropicrin poisoning is to bleed one-half of one per cent of the body weight as soon as possible after gassing and then to administer at once water by way of the mouth. Additional fluid may be supplied later by intravenous infusion of sodium chloride solution in accordance with hemoglobin readings and temperature changes. With this treatment there are no delayed deaths (117).

USES

One milligram of chloropicrin in one liter of sugared must retards fermentation, and 5 to 6 mg. stops fermentation entirely. One milligram per liter will prevent the growth of *Saccharomyces vini* (118). Twenty to 30 mg. of chloropicrin per liter stops lactic acid fermentation; 50 to 60 mg. of chloropicrin per liter stops the ammoniacal fermentation of urine; and 0.1 mg. of chloropicrin per liter stops all development of the bacteria of sorbose (119).

Mercandier (120) found chloropicrin to be bactericidal to *B. coli* and streptococcus; a saturated atmosphere of chloropicrin kills the bacilli in less than twenty-four hours in the light at the temperature of the labora-

tory. The spore of *B. anthracis* is killed in a saturated atmosphere of chloropicrin in from six to fourteen hours at 17–18°C., whereas *B. subtilis* is only slightly attacked after forty-eight hours.

An aqueous solution of chloropicrin (1.6 g. per liter) was found by Violle (121) to possess high antiseptic power. At the rate of 12 mg. per liter of bouillon, chloropicrin prevents the growth of *B. coli, B. typhosus, B. paratyphosus,* staphylococcus, streptococcus, and other non-spore-forming bacteria. At the rate of 24 mg. per liter of bouillon, chloropicrin prevents the growth of *B. subtilis.* Emulsions of *B. coli, B. typhosus, B. paratyphosus, B. dysentericae, B. proteus,* and *B. pyocyaneus* are killed after a 30-minute contact with chloropicrin, and *B. subtilis* is killed after contact for one hour. Chloropicrin retains its bactericidal power for several hours (in contradistinction to chlorine, iodine, and their derivatives) and does not coagulate egg albumen and other protein bodies.

Randier (122) showed that cultures of *B. paratyphoid, B. Yersin,* and *B. Eberth* failed to grow after having been exposed to chloropicrin vapor.

When tested by the wet filter paper method, Reddish (123) found that chloropicrin killed both *B. typhosus* and *M. aureus* in 15 minutes.

It was found by Shufflebotham (124) that chloropicrin was very effective against *B. influenzae.*

A great deal of experimentation has been done with chloropicrin on insects and favorable results have been reported on the following: *Acarapis woodi* (125), *Agriotes* (126), *Agriotis segetum* (127), *Aleurobius farinae* (128), *Aleyrodes vaporariorum* (129), *Anobiids* (130), *Anobium hirtum* (131), *Anopheles maculipennis* (132), ants (133), aphis (134), arachnid (131c), *Argas reflexus* (135), *Blattella germanica* (136), *Bombyx mori* (137), *Bombyx neustria* (138), *Bruchus chinensis* (139), *Bruchus obtectus* (140), Buffalo carpet beetle (141), cabbage root fly (134b), *Calandra granaria* (142), *Calandra oryza* (143), *Callipterus italicus* (144), *Ceratophyllus fasciatus* (145), *Cerocipidae* (127b), *Ceroplastes rusci* (146), *Charancons* (147), *Chrysomyia macellaria* (148), *Cimex lectularius* (149), *Cochliomyia macellaria* (150), *Coraebus rubi* (151), *Criocephalus rusticus* (152), *Culex pipiens* (132), *Dendrolimus pini* (136d), *Dermestes vulpinus* (153), *Diaspis pentagona* (146), *Dociostaurus maroccanus* (154), *Doryphora* (155), *Echocerus cornutus* (156), *Ectobia lividia* (157), *Ephestias* (147a), *Ephestia kuehniella* (158), *Epitrix cucumeris* (129), fleas (159), flies (160), fur parasites (159c), *Galleria mellonella* (161), *Gelechia gossypiella* (152), *Geometrid larvae* (127b), grain insects (162), grasshoppers (163), *Heterodera* (164), *Hylotrupes bajulus* (152), *Jassidae* (127b), *Laemophaleus ferrugineus* (165), *Laemophaeus minutus* (129), *Lecanium hesperidum* (146), *Lepism* (166), *Leptinotarsa decemlineata* (167), *Leucotermes lucifugus* (168), *Liparis chryssorrhoea* (146), *Lucilla* (150b), *Malacosoma neustria* (136d), *Melolontha*

vulgaris (169), *Microgaster glomeratus* (170), *Monomorium pharaonis* (171), *Muca domestica* (172), *Myzus persicae* (129), *Nematodes* (173), *Nuptus hololeucuc* (174), *Otiorhynchus cingulatus* (166), *Otiorhynchus sulcatus* (175), *Oxythyrea hirta* (170), *Pachymerus chinensis* (129), *Palomona viridissima* (166), *Pectinophora gossypiella* (176), *Pediculus humanus* (177), *Periplaneta* (136), *Phlorimaea opercuella* (152), *Phorbia ceparum* (134b), *Phthorimaea opercuelella* (176), *Phyllodromia germanica* (136d), *Pieris brassicae* (170), *Pieris rapae* (166), *Platyedra gosspiella* (178), *Plodia americana* (179), *Plodia interpunctella* (180), *Polychrosis botrana* (181), *Rhizopertha dominica* (129), rice insects (182), scale (134c), *Schistocerca tatarica* (144), *Silvanus surinamensis* (183), *Sirex juvencus* (152), *Sitodrepa panicea* (127b), *Sititroga cerealella* (184), *Souris* (147), *Sparganothis pilleriana* (134b), *Stephanoderes coffea* (185), *Strachia conata* (166), *Tar-*

TABLE 12

Action of chloropicrin on fungi

	TIME						
	7 minutes	15 minutes	30 minutes	60 minutes	210 minutes	340 minutes	480 minutes
Amblyosporium					−	−	+
Botrytis cinera	−	−	−	−	+	+	+
Chaelomium bostrychodes					−	−	+
Hypomyces ochracea	+	+	+	+	+	+	+
Mucor mucedo	−	−	−	−	+	+	+
Nocardia	−	−	−	−	−	−	+
Penicillium	−	−	−	−	−	−	+

+ indicates that death of the organism resulted from that exposure.

sonemus (129), *Tenebrio molitor* (186), *Tenebrionid* (166), *Tenebroides mauritanicus* (187), *Tenthredinid* (178), tent caterpillar (188), *Tetranychus bumaculatus* (189), *Tetranychus telarius* (190), thrips (127b), timber insects (191), *Tinea granella* (192), *Tinea pellionella* (157), *Tineola biselliellela* (193), *Trialeurodes vaporariorum* (194), *Tribolium confusum* (195), *Tribolium ferrugineum* (129), *Tribolium navale* (196), *Trichophaga tapetzella* (157), *Trogoderma granarium* (197), *Trogoderma khapra* (198), *Tyroglyphus farinae* (139), *Tyroglyphus mycophagus* (195a), weevils (199).

Matruchot and See (200) obtained the results shown in table 12 using a saturated atmosphere of chloropicrin on the fungi growing in culture tubes.

Bertrand (201) found that chloropicrin has the same effect upon plants in the dark as in diffused daylight, but in the direct sunlight the injury is much greater. Humidity does not affect the activity of chloropicrin vapor on plants. The influence of temperature is very distinct. If the differ-

ences of treatment are too great, the effects of chloropicrin are almost proportional to the concentration of the vapor and the duration of the exposure; that is, a 20-minute exposure to a concentration of 30 g. gives the same result as a 30-minute exposure to 20 g. Tests were made with the leaves of the following species: Japanese spindle tree, black poplar, lilac, pear tree, elm, melilot, and golden daisy.

Chloropicrin has been used successfully as a fumigant on a number of other plants: apple tree (202), aster (127b), beans (134b), begonia (127b), cabbage (134b), camelia (146), coleus (127b), cottonseed (176), daisy (127b), dandelion (127b), date (203), dock (127b), edible mushroom (204), geranium (127b), Japanese spindle wood (27), jasmine (146), legumes (169), myrabolan (146), onions (134b), orange tree (205), plum tree (206), poplar (138), potatoes (152), roots (126b), rose (207), saliva (127b), tomato plants (208), vine grafts (169), weeds (209), willow boughs (127b), wild cherry (134c), wild quince (146), wild vetch (127b).

Cats gassed with chloropicrin in such concentrations that death generally results within 4 days usually exhibit a marked generalized analgesia, both superficial and deep. Gassed cats react with no obvious sign of pain to operative interferences, including laparotomy and gentle friction of the parietal peritoneum. The analgesia develops within a few hours after gassing and reaches its maximum in about twenty-four hours. With chloropicrin practically normal sensitiveness has been observed seven days after gassing. This analgesia is considered to be caused and maintained largely by a general, low-grade tissue asphyxia, which is chiefly of pulmonic origin. In most instances death occurred within forty-eight hours after gassing, 1 part to 10,000, for 30 to 60 minutes (210).

Winternitz, Finney, and Wislocki (211) show the comparative toxicology of chloropicrin for the rabbit, dog, cat, monkey, goat, rat, and guinea pig. Florentin (212) determined the toxic dose of chloropicrin for a dog to be 0.5 gram.

Experiments made with goats, sheep, and cattle on the ranges have shown that small quantities of chloropicrin in mineral oil, or in pine tar oil, are very effective in repelling flies, and that wounds treated with the mixture appear to heal rapidly (213).

Earthworms and millipedes were killed to a depth of 5 inches in soil after exposure for 1.5 hours to a concentration of chloropicrin, 8.7 oz. per 1000 cu. ft. at 55.4°F., relative humidity at 88 (127). Chloropicrin is of great value as a partial sterilizing agent. It is fatal to eelworms and wireworms and harmless to plants; indeed, it promotes root action to a remarkable degree (214).

Bertrand and Dassonville (215) recommend that chloropicrin be substituted for sulfur dioxide in the treatment of mange (gale) in horses. Excellent results are said to be obtained.

A water solution of chloropicrin (10 to 20 mg. per liter) is very toxic to amoeba, vorticella, and paramecium. It is suggested that chloropicrin be used for partial sterilization of stools (134a).

Field mice have been successfully exterminated by Ringelmann (216) and Vayssière (217) with the use of chloropicrin. Rats have been successfully exterminated by the use of chloropicrin (218). Encouraging results have been obtained by Lormand (219) in tests with chloropicrin for the destruction of foxes and by Traunt (220) in the extermination of the Siberian marmot.

A viper resisted the action of chloropicrin at the rate of 30 cc. per cubic meter for 7 minutes, then died (170).

Billon (221) obtained, on October 16, 1926, French patent No. 612,075 for the purification of vaccines by means of chloropicrin.

Chloropicrin has been recommended for use as a warning agent for illuminating gas or with hydrocyanic acid when used as a fumigant (222).

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