Thermal Stability of Methyl Chloroform and Carbon Tetrachloride

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THE possible formation of phosgene when chlorinated hydrocarbons are heated in air has been given much publicity and many papers have dealt with this problem. Among these may be mentioned the work of Biesalski (*4*) on the decomposition of chlorinated methane, ethane, and ethylene compounds when heated over copper oxide, metal chlorides, and various other substances. In every case carbon tetrachloride produced the most phosgene, yielding as much as 25% by weight when passed over copper chloride at 482° F.

In 1941 Dachlauer (*6*) mixed vapors of chlorinated hydrocarbons with air and passed the mixture through a tube of iron nails heated to 932° F. Carbon tetrachloride was reported to yield the highest percentage of phosgene and the extent of phosgene formation decreased with decreasing chlorine content in the chloromethane compounds. Much smaller amounts of phosgene were produced by the chloroethane compounds.

A recent thorough investigation by Sjöberg (*7*) has verified the earlier work and extended it to other compounds and other metals. He studied the products obtained from vapors of carbon tetrachloride, chloroform, trichloroethylene, perchloroethylene, dichloroethane, tetrachloroethane, pentachloroethane, and hexachloroethane in contact with heated copper, aluminum, and zinc from 212° to 932° F. He found that carbon tetrachloride produces much larger quantities of phosgene and decomposes at lower temperatures than the other chlorinated hydrocarbons. Chlorinated ethanes which contain at least one hydrogen atom produced hydrogen chloride more readily than did carbon tetrachloride, chloroform, or hexachloroethane. Sjöberg correctly pointed out that in all cases, except that of carbon tetrachloride, hydrogen chloride will act as an olfactory warning agent long before enough phosgene has formed to become dangerous.

Methyl chloroform (1,1,1-trichloroethane) is similar to carbon tetrachloride in its physical and solvent characteristics but in higher concentrations can be tolerated in the atmosphere (*1–3*). Consequently, it is replacing carbon tetrachloride in many types of cleaning applications. As no data on its stability appear to have been published, the authors have studied its decomposition on various metals as a function of temperature. Tests have been carried out with technical methyl chloroform and with a formulation (Chlorothene) containing inhibitors to prevent the reaction of liquid methyl chloroform with aluminum. Carbon tetrachloride was also studied for comparison.

EXPERIMENTAL TECHNIQUE

The apparatus (Figure 1) is made up of an air-flow regulator, a vaporization chamber, two U-tubes, three gas-absorption bubblers, and a wet-test meter. Air is brought in under pressure through the air-flow regulator, which consists of a manometer across a capillary tube. The stream is directed toward the bottom of the vaporization chamber, a 250-ml. round-bottomed flask equipped with a dropper on top. The compound to be tested is introduced through this dropper at such a rate that a 1.00-ml. sample is vaporized while roughly 20 liters of air passes through the system. The solvent vapor–air mixture passes through the first U-tube, which is filled with small pieces of the metal under observation. This tube is immersed in a constant temperature bath of Wood's metal. The reaction products pass

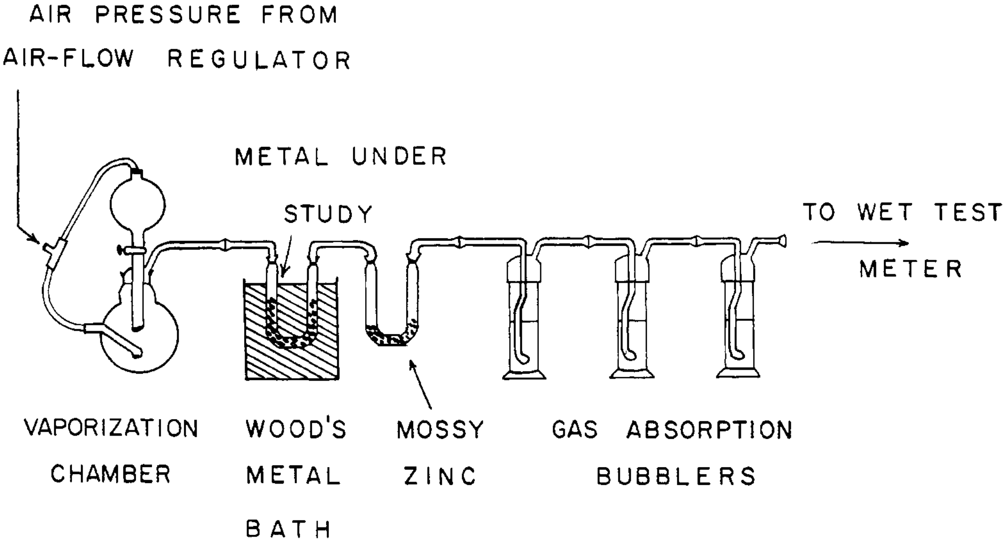

Figure 1. Apparatus for thermal decomposition of chlorinated hydrocarbons on metals

through a second U-tube, which is filled with mossy zinc (to remove hydrogen chloride) when phosgene is being determined, but is empty when hydrogen chloride is sought. The remaining gases are passed through gas-absorption bubblers. The absorption medium for phosgene is aniline in water, while that for hydrogen chloride is $0.1N$ sodium hydroxide. Finally the gas passes through a wet-test meter. Thirty-three liters of gas is passed in each case.

Phosgene reacts with aniline to produce 1,3-diphenylurea, which can readily be determined by ultraviolet spectrophotometry (*5*). Acetyl chloride, if present, is hydrolyzed and does not interfere. Hydrogen chloride is determined by titrating the excess sodium hydroxide with standard $0.1N$ hydrochloric acid. The hydrogen chloride results are high when large amounts of phosgene are present.

The recovery of phosgene was checked by breaking ampoules containing weighed amounts of phosgene, sweeping the phosgene vapor through the apparatus with air, and determining the quantity of diphenylurea formed. Results obtained with no metal in the system have been reported (*5*). Recoveries ranged from 96 to 100% and indicated that the amount of phosgene decomposed or lost in the apparatus was negligible.

All the metals used are available commercially. Purified copper pellets and analytical reagent mossy zinc were procured from the Mallinckrodt Chemical Works. Aluminum foil was obtained from the Reynolds Metals Co. The cast iron (used in the form of turnings) was found to contain 3.2% carbon; spectrographic analysis showed the following percentages: manganese 0.6, chromium 0.1 to 0.2, nickel 0.04, copper 0.03, and silicon 1 to 5. Steel, in the form of cold-roll 1045, contained 0.15% carbon and the following percentages by spectrographic analysis: manganese 0.6, chromium 0.07, nickel 0.003, copper 0.03, and molybdenum 0.05 to 0.1. The yellow brass was found to contain 0.1 to 1% lead and 0.01 to 0.1% iron by spectrographic analysis in addition to its nominal proportions of 67% copper and 33% zinc.

RESULTS

In agreement with the results of Sjöberg (*7*) and others, carbon tetrachloride was found to produce more phosgene than other chlorinated solvents when the vapors are passed over heated metal. This effect is particularly great with cast iron, with which 1 gram of carbon tetrachloride yields 275 mg. of phosgene at 635° F. (see Table I). Under the same conditions methyl chloroform produces only 0.74 mg. of phosgene; methyl chloroform, however, yields more hydrogen chloride. Carbon tetrachloride also produces large amounts of ferric chloride.

Table I. Decomposition Products of Some Chlorinated Solvents with Cast Iron

Temp., ° F.	Decomposition Product	Milligrams per Gram of Solvent		
		Uninhibited methyl chloroform	Inhibited methyl chloroform[a]	Carbon tetrachloride
300	Phosgene	0.007	0.000	0.48
405	Phosgene	. . .[b]	0.016	8.87
435	Phosgene	0.049	. . .	. . .
460	Phosgene	0.083	0.014	52.9
540	Phosgene	. . .	0.27	133
555	Phosgene	0.58	. . .	. . .
635	Phosgene	0.74	0.78	275
755	Phosgene	. . .	0.84	. . .
540	Hydrogen chloride	143	201	56.6

[a] Chlorothene produced by Dow Chemical Co.
[b] Where blanks are shown, no tests were made.

The thermal decomposition of carbon tetrachloride in contact with steel was much less than with cast iron. The explanation for this is not apparent and has not been investigated.

The thermal decomposition of carbon tetrachloride with copper also produces large yields of phosgene, as shown in Table II. Appreciable quantities were observed at temperatures as low as 395° F. At temperatures below 600° F. methyl chloroform produces small amounts of an unknown compound which reacts with aniline to form a material similar in its ultraviolet absorption characteristics to that of acetanilide or α-chloroacetanilide. Above 600° F. only trace quantities of phosgene are formed. Again methyl chloroform produces more hydrogen chloride, but the quantity appears to be diminished by the presence of inhibitor in this case.

Table II. Decomposition Products with Copper

Temp., ° F.	Decomposition Product	Milligrams per Gram of Solvent		
		Uninhibited methyl chloroform	Inhibited methyl chloroform	Carbon tetrachloride
395	Phosgene	. . .	. . .	7.10
460	Phosgene	0.00	. . .	. . .
465	Phosgene	. . .	0.00	. . .
470	Phosgene	. . .	. . .	36.4
545	Phosgene	0.00	. . .	. . .
560	Phosgene	. . .	0.00	. . .
695	Phosgene	0.34	0.39	. . .
540	Hydrogen chloride	177	34.7	29.0

Carbon tetrachloride and methyl chloroform are only slightly decomposed in contact with zinc, aluminum, and brass (Table III). Phosgene formation is always greater for carbon tetrachloride, while hydrogen chloride formation is greater for methyl chloroform.

Table III. Decomposition Products

Temp., ° F.	Decomposition Product	Milligrams per Gram of Solvent		
		Uninhibited methyl chloroform	Inhibited methyl chloroform	Carbon tetrachloride
	With Zinc			
300	Phosgene	. . .	. . .	0.020
460	Phosgene	0.15	0.11	0.37
635	Phosgene	. . .	1.92	5.60
640	Phosgene	1.45	. . .	. . .
540	Hydrogen chloride	6.66	6.64	1.98
	With Aluminum			
295	Phosgene	0.083	. . .	0.048
460	Phosgene	0.045	. . .	0.075
670	Phosgene	0.056	0.27	0.34
540	Hydrogen chloride	2.49	2.21	0.73
	With Brass			
450	Phosgene	0.14	0.033	0.70
670	Phosgene	0.30	0.17	5.43
540	Hydrogen chloride	8.90	6.08	0.83
	With Steel			
460	Phosgene	0.10	. . .	0.50
540	Phosgene	0.22	. . .	1.68
670	Phosgene	0.33	. . .	5.72
540	Hydrogen chloride	195	166	8.52

It is interesting to note the small amounts of decomposition products formed on aluminum. This unexpected result can possibly be ascribed to an oxide film protecting the aluminum. After the runs the metal was still bright, showing no evidence of having been attacked. The metal was not kept in contact with a liquid phase in these tests; aluminum is known to react with many chlorinated aliphatic liquids.

COMPARISON WITH LITERATURE DATA

A great many variations are possible in a study such as this. The principal differences between the reported work and that of Sjöberg are three: (1) Sjöberg used dried air, but the authors made no attempt to control the humidity. (2) Sjöberg used a straight glass tube for his metal bed, whereas a U-tube was used

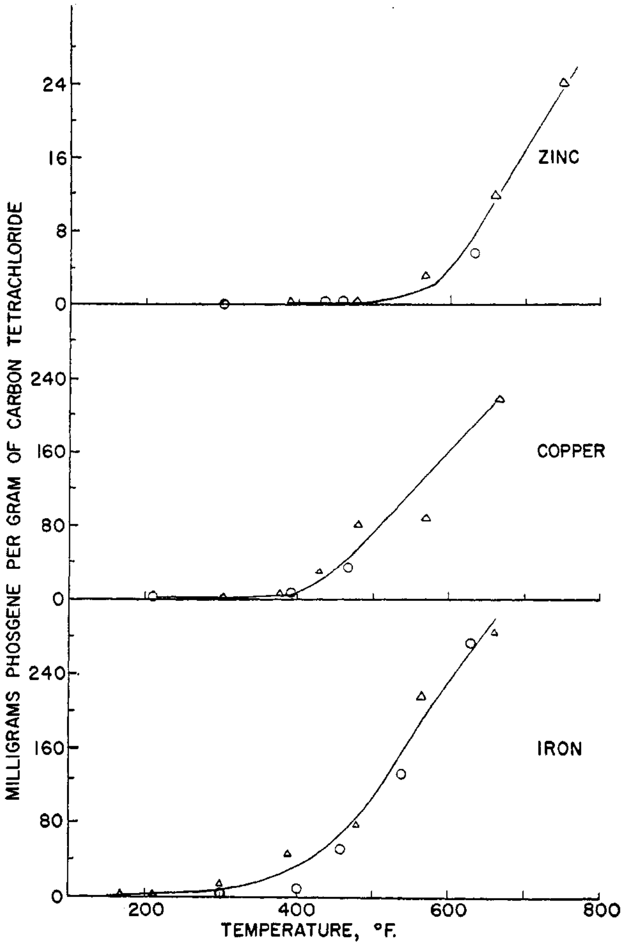

Figure 2. Phosgene formation from carbon tetrachloride

△ Data from Sjöberg (7)

in the present tests. (3) Sjöberg used a bed of antimony to remove any chlorine which may have formed. A small amount of chlorine does not interfere with the analytical method used by the authors and hence was not removed.

Sjöberg's phosgene results on carbon tetrachloride are graphically compared with those of the authors in Figure 2. The remarkable agreement indicates that, except possibly at low temperatures, humidity has very little influence on the extent of phosgene formation.

Table IV lists the amounts of phosgene formed when various chlorinated hydrocarbons are passed over iron at 635° F. Carbon tetrachloride forms at least 100 times as much phosgene as any of the other chlorinated hydrocarbons. Methyl chloroform is much less readily decomposed to phosgene and compares favorably with such solvents as perchloroethylene and trichloroethylene.

Table IV. Phosgene Formation from Thermal Decomposition of Chlorinated Hydrocarbons on Iron at 635° F.

Chlorinated Hydrocarbon	Mg. Phosgene/G. Solvent
Carbon tetrachloride	275
Carbon tetrachloride	265[a]
Chloroform	2.4[a]
Dichloroethane	0.7[a]
Hexachloroethane	0.0[a]
Methyl chloroform	0.74
Methyl chloroform (Chlorothene)	0.78
Pentachloroethane	1.4[a]
Perchloroethylene	0.1[a]
Tetrachloroethane	0.6[a]
Trichloroethylene	2.3[a]

[a] Data from Sjöberg (7).

For purposes such as metal cleaning, the volume of solvent used is likely to be of more interest than the mass. Because of density differences, the foregoing comparisons turn out even more favorably for methyl chloroform if the data are based on the volume of liquid vaporized. The density of methyl chloroform at 25° C. is 1.325.

SUMMARY

The thermal stabilities of methyl chloroform and carbon tetrachloride vapors, in contact with heated metals in air, have been investigated and compared with literature data. With respect to phosgene formation at temperatures up to 700° F., methyl chloroform is one of the more stable chlorinated aliphatic hydrocarbons. Considerable amounts of hydrogen chloride are obtained from methyl chloroform passed over iron, steel, or copper at 540° F.

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