Stability of Trichlorofluoromethane in the Presence of Moisture and Certain Metals

JAMES M. CHURCH and JOSEF H. MAYER[1]
Department of Chemical Engineering, Columbia University, New York, N. Y.

CHLORO-FLUORO derivatives of methane and ethane are volatile and nontoxic compounds. Consequently they have found wide use as refrigerants since the early thirties, and are known commercially under the trade names Freon, Unitron, Genetron, and Isofron. More recently they also have been employed as propellants in the so-called Aerosol formulations for dispensing insecticidal and cosmetic preparations.

Although these compounds are claimed to be stable and noncorrosive in general, the individual chlorofluorohydrocarbons show a variation in their stability.

Trichlorofluoromethane (CCl_3F), a widely used industrial refrigerant, is somewhat unstable under certain conditions encountered in refrigerating systems, causing extensive corrosion, which interferes with the proper operation of the equipment.

The purpose of this investigation was to determine the stability and corrosive behavior of trichlorofluoromethane in the presence of moisture and in contact with various metals under simulated refrigeration conditions in order to obtain specific information on proper conditions for the use of this compound in refrigeration equipment.

LITERATURE SURVEY

Few published reports are to be found concerning the instability of chlorofluorohydrocarbons or the corrosive action from the resulting decomposition products. The first of these compounds developed commercially was dichlorodifluoromethane, which has been the most thoroughly investigated. Evidently pure dry vapor of Cl_2CF_2 did not attack the ferrous metals or lead-tin solders commonly found in most refrigeration equipment, even at 350° F. (*8*). However, most bronzes, brasses, and magnesium alloys were attacked by the hot vapors. When various metal test specimens were sealed in glass capsules half filled with the dry liquid Cl_2CF_2 and heated to 235° F. continuously for five months, very little evidence of corrosion occurred (*11*). Only a slight discoloration occurred on the surface of the aluminum, copper, bronze, lead, and zinc specimens. However, when magnesium alloys were exposed to Cl_2CF_2 saturated with water in sealed tubes at 235° F. considerable corrosion was noted. At higher temperatures within the range of 1050° to 1400° F. the vapors of Cl_2CF_2 readily attack most metals (*2*). Other experiments included long exposure of 21 common metals in contact with the dry liquid and vapor at room temperature for one year, noting any corrosion and checking for any loss in tensile strength (*3*). No measurable effects were detected in any of the specimens. At higher temperatures of 400° F. tin-lead (60 to 40) solder showed some corrosion, and at 780° F. copper was attacked. In another set of tests various metal specimens in contact with the liquid Cl_2CF_2 in glass sealed tubes were heated intermittently from room temperature to 225° F. In some of the tests small amounts of water were added to the Cl_2CF_2. Only in the latter instances was any corrosion noted, especially with the iron and the tin-lead solder specimens (*5*). Other chlorofluorohydrocarbons similarly tested included monochlorodifluoromethane, trichlorofluoromethane, difluoroethane, monochlorodifluoroethane, and dichlorotetrafluoroethane as aqueous and alcoholic solutions in contact with steel and aluminum metal specimens at 130° F. (*9*). Corrosion occurred in all cases, with trichlorofluoromethane showing the greatest amount of corrosion.

The chemistry of the fluorohydrocarbons has been studied extensively and is well summarized by Henne (*7*). The monofluorides are characterized by their relative instability and tendency toward dehydrofluorination. In contrast, the polyfluorohydrocarbons are stable, unreactive, and resistive to oxidation. Mixed polyhalogenohydrocarbons containing both chlorine and fluorine attached to the same carbon atom are less stable than the polyfluoro derivatives. The difference in the stability of the various chloro-fluoro hydrocarbons may be explained in terms of the bond distances of the C—F and C—Cl bonds in the various combinations. An increase in the number of fluorine atoms considerably shortens the bond distances of both the C—F and C—Cl bonds as shown in Table I.

Table I. Atomic Distances in Angstrom Units (*7*)

Compound	C—F Bond	C—Cl Bond	Compound	C—F Bond	C—Cl Bond
CCl_4	...	1.76	$CHCl_3$	...	1.77
CCl_3F	1.40	1.76	$CHCl_2F$	1.41	1.73
CCl_2F_2	1.35	1.70	$CHClF_2$	1.36	1.73
$CClF_3$	1.35	1.70	ChF_3	1.35	...
CF_4	1.36	...			

EXPERIMENTAL PROCEDURES

The stability tests performed in this investigation were designed to simulate closely the conditions that prevail in industrial refrigeration systems. The conditions for exposure of trichlorofluoromethane to metals included: a "dynamic" state with constant motion of the refrigerant in contact with the metal, a relatively large surface area of the metal in the form of shavings, and addition of definite quantities of moisture and air which are generally found present in refrigeration systems.

The exposures were made in cylindrical pressure bombs, 12 inches long by 3 inches i.d., with wall thickness of about

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[1] Present address, Trubek Laboratories, East Rutherford, N. J.

1 inch as shown in Figure 1. The bombs with flange and a removable cover plate were made of cast iron, cast steel, aluminum, and copper. The ¼-inch pipe nipples, both on the bottom of the bomb and the cover plate, were of the same material as the bomb in the steel and copper bombs. However, ¼-inch stainless steel nipples (Type 304) replaced the original nipples of the cast iron and aluminum bombs which proved too weak to withstand the stress of tightening the fittings. A ¼-inch stainless steel (Type 304) cap was placed on the nipple of the cover, while a ¼-inch stainless steel needle valve (Hoke Inc., Englewood, N. J., Type 344) was attached to the nipple on the bottom of the bomb. Leak Lock B (Highside Chemicals Co., Clifton, N. J.) was used as the sealing compound on the threaded joints, with excellent results. A $\frac{1}{64}$-inch thick Teflon gasket was inserted between the body and the cover plate.

The bombs were supported on a rack 32 inches long, 17 inches wide, and 4 inches high; constructed of 1 × 1 × $\frac{3}{16}$-inch angle iron; and contained four pairs of bearings for mounting of four bombs simultaneously. The bombs were placed horizontally on the rack with the bottom and top nipples resting on the bearings, and were rotated at 60 r.p.m. by belts driven by an electric motor. A hood built of an iron framework covered with ¾-inch thick Cellotex was placed over the rack containing the bombs. Four 250-watt infrared lamps controlled by rheostat were attached to the inside of the hood for heating the enclosure during the test runs.

The cleaned and dried bombs were prepared for exposure, by first filling them about half full with clean dry metal shavings, closing the bomb, evacuating the air by use of a high vacuum pump to 2 mm. of mercury pressure, then adding measured amounts of water and dry air, and a definite amount of trichlorofluoromethane into the evacuated bombs. The filled bombs were then placed on the rack and rotated at the desired temperature for a specified period of time. At the end of the exposure the bombs were removed from the rack, and the contents removed for analysis to determine the degree of decomposition of trichlorofluoromethane. The tests were made at 150° F. to determine the effects of moisture and air on the rate of decomposition of trichlorofluoromethane. Moisture contents of 0.01 to 0.13% by weight and air volumes of 1 to 4% by volume of the gas in the free space were investigated. In most instances, exposure times of 4½ days or 108 hours were sufficient to determine the extent of decomposition.

ANALYTICAL PROCEDURES

The objective of the investigation was to obtain the rate of decomposition of trichlorofluormethane in the presence of moisture, air, and certain metals at 150° F. Any decomposition of the trichlorofluoromethane in contact with the metal and moisture may result in elimination of at least one of the halogens from the trichlorofluoromethane molecule. Therefore, by measuring the amount of halogen released, the amount of decomposition could be determined. The decomposition products might be present in several forms. By the interaction of the halogen with the metal an inorganic halide could be formed, which probably would be insoluble in the liquid trichlorofluoromethane, and therefore could be separated as a solid. Any hydrolytic action of the moisture with the trichlorofluoromethane would form a hydrogen halide which probably would be present in the vapor phase. The hydrogen halide probably would also attack the metal and thus form the halide salt of the metal by a secondary reaction. A more remote possibility would be the presence of the halogen in the free molecular state.

Of the two types of halogen present in the trichlorofluoromethane molecule, chlorine probably would be more reactive than fluorine.

In the preliminary test runs no free halogen or halogen halide was found in either the liquid or vapor, following the exposure of the trichlorofluoromethane. Instead, any halogen resulting from the decomposition of the trichlorofluoromethane actually reacted with the metal, and was present as a halide salt. Accordingly, analytical methods for determining quantitatively both fluoride and chloride present in the decomposition products were developed. Tests for the presence of fluoride proved negative in all cases.

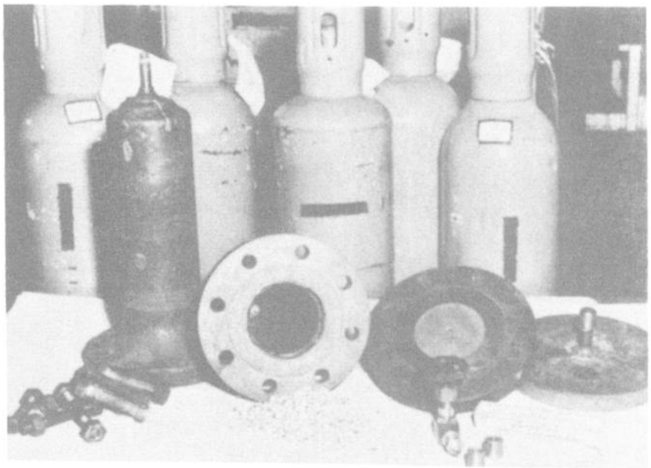


Figure 1. Dissembled test bombs in Foreground with tanks of trichlorofluoromethane in Background

Determination of Amount of Chloride Decomposition Products. The bomb was removed from the rotating rack, was cooled to room temperature, and then placed with the valve in the upward position. Glass tubing in the shape of an inverted U was attached to the valve and a little of the trichlorofluoromethane vapor was transferred to a cooled test tube containing some methanol chilled in an ice bath. The resulting solution was then tested for chloride ion by adding drops of concentrated silver nitrate solution in methanol. Upon standing a couple of minutes any turbidity would indicate as little as 2 p.p.m. of chloride ion in the solution. The test proved negative, denoting the absence of any hydrogen chloride in the vapor phase. The bomb was further chilled, then inverted, the valve opened, the liquid removed, and filtered through filter paper for the removal of a mixture—metal shavings, fine metal particles, and inorganic chloride. The solid mixture was added to the wash water used to flush out the bomb, following the removal of the trichlorofluoromethane. A sample of the filtered trichlorofluoromethane liquid was tested with alcoholic silver nitrate solution for the presence of any dissolved chloride; the test was always negative, indicating the metal chloride formed to be too insoluble in the trichlorofluoromethane for detection.

Following the removal of the trichlorofluoromethane the bomb was opened. The inside of the bomb and the fittings were then flushed with hot distilled water until no more chlorides could be detected in the washing. The combined washings were made alkaline to phenolphthalein with dilute sodium hydroxide solution to precipitate any dissolved metal present. The precipitate in the iron bombs was green, bulky ferrous hydroxide which upon heating turned to a heavy black suspension. Any dissolved aluminum, lead, or tin was also precipitated in the form of the hydroxides. The concentrated washings were cooled and aliquots taken for analysis of chloride content by the Mohr method (*12*), using 0.02*N* silver nitrate solution for titration and 4% potassium chromate solution as indicator.

Any fluorides present in the concentrated aqueous solution were determined using a spot test method (*6*). It produces a color change from red-violet to the faint yellow of a zirconium alizarinate complex, formed with the fluoride ion in the presence of concentrated acetic acid. The test is capable of detecting as little as 20 p.p.m. of fluoride. No positive test for fluoride was obtained in any of the decomposition products.

Determination of Moisture Content in Trichlorofluoromethane. During the investigation the moisture content of the starting material (as supplied in 25-pound cylinders) was checked. The first method employed absorption of the water with phosphorus pentoxide (*4*), but failed to give reproducible results. However, a spectrophotometric method (*1*) using infrared gave accurate and reproducible results. This method is based on the fact that trichlorofluoromethane does not absorb at a wave length of 2.67 microns, where water has a considerable absorption maximum. The absorption of water closely follows Beer's law. Either gas cells with a very long path, or liquid cells with a considerably shorter path can be employed satisfactorily to measure the absorption. Pressure cells for both vapor and liquid were constructed as shown in Figure 2. The liquid cell consisted of a stainless steel cylinder 90 mm. long and 45 mm. i.d. Two ⅛-inch stainless steel needle valves were mounted on the side of the cylinder for charging and discharging the cell. Polished sodium chloride windows (The Harshaw Chemical Co., Cleveland, Ohio) 50 mm. in diameter by 6 mm. thick were attached to the cell by a brass screw cap, using 1⁄64-inch thick polyethylene gasket on the inside and a 0.5-mm. thick neoprene gasket on the outside of the salt window. Measurements were made with a Model 12 B Perkin-Elmer infrared spectrometer remodeled for double-beam action (*10*). A calibration curve was made with samples of trichlorofluoromethane containing known amounts of moisture and recording the amount of absorption of each at 2.67 microns. For example, a sample containing 60 p.p.m. of moisture was prepared by first filling a copper bomb with a definite amount of trichlorofluoromethane, chilling the contents of the bomb considerably below the boiling point of the liquid, and then adding a weighed amount of water directly to the chilled trichlorofluoromethane. The bomb was closed and the contents were mixed by rotating the bomb at room temperature for several hours to dissolve the water completely in the trichlorofluoromethane. Other samples with a lesser amount of moisture were prepared by dilution of the first sample with fresh trichlorofluoromethane.

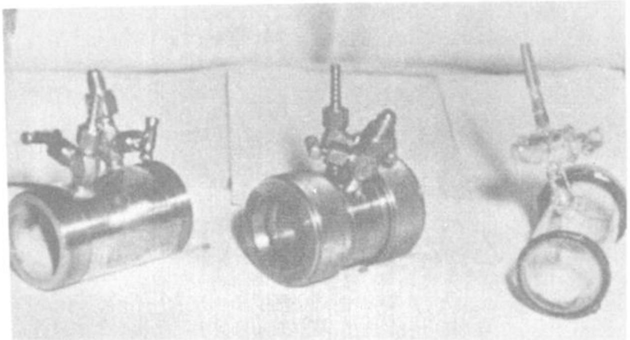


Figure 2. Infrared cells for water determination of vapor and liquid samples of trichlorofluoromethane

Samples of the liquid containing known amounts of moisture were introduced into the previously evacuated cell through one of the needle valve openings. Since the moisture content in the original trichlorofluoromethane was not known, it was possible to calculate this from the absorption measurements by extrapolation, using Beer's law. For I_0 the per cent absorption at zero level, the absorption was measured with the empty evacuated cell. This was necessary since it was impossible to prepare a sample of absolutely dry (0 p.p.m. water) trichlorofluoromethane. A fairly good calibration curve was obtained in this way, which was similar but not identical to that of Benning and others (*1*).

The above method was considered sufficiently accurate for the purpose, since the moisture content in the original material in all cases was less than about 10 p.p.m. In all of the stability tests, the water content added was more than 100 p.p.m.

DISCUSSION OF RESULTS

Effect of Moisture Content. Trichlorofluoromethane containing moisture from 0.001 to 0.123 weight % and 4 volume % air, was exposed in the presence of a large surface area of cast steel and cast iron for 108 hours at 150° F. Increasing amounts of moisture added to the trichlorofluoromethane greatly increased the rate of decomposition (Figure 3). However, the rate was not strictly linear, as noted from the tendency of the curve to flatten out. Even at the lowest concentrations of only about 0.001 weight % (10 p.p.m.) of moisture, some decomposition occurred. In the higher range of moisture contents the decomposition of the trichlorofluoromethane increased much less, indicating that the moisture content is only one of the factors governing the rate of decomposition. For example, the decomposition rate with over 1.0% of added water was only about three times as much as when 0.123 weight % water was used (3.76 *vs.* 1.32%, respectively).

Effect of Air. Additions of 1, 2, and 4% by volume of added air, with approximately the same moisture content present, had practically no effect upon the extent of the decomposition of the trichlorofluoromethane over this wide range of contamination.

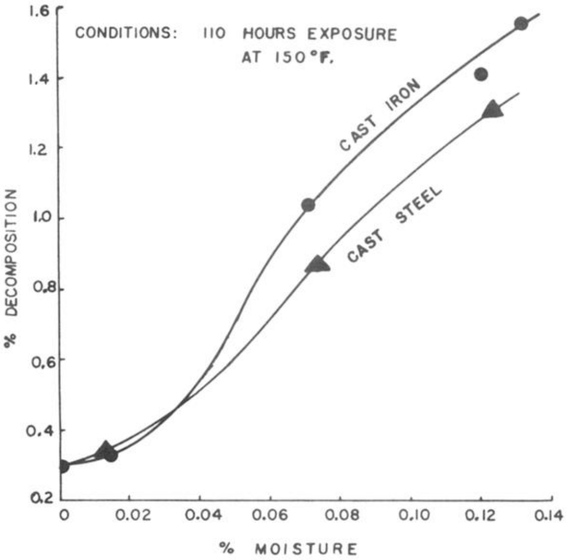


Figure 3. Effect of moisture on the decomposition of trichlorofluoromethane

Effect of the Metals. The following metals, alloys, and combinations of metals were employed: cast iron shavings and bomb; cast steel shavings and bomb; aluminum shavings and bomb (Alcoa No. 355 casting aluminum alloy, 92.4% Al, 5.0% Si, 1.2% Cu, 0.5% Mg, 0.3% Mn, 0.3% Fe, 0.2% Zn and traces Ti, Ni, etc.); copper shavings and bomb; lead liner in copper bomb; bronze I shavings in copper bomb (bronze I = 75.5 to 78.5% Cu, 7.25 to 8.75%

Sn, 13.5 to 16.5% Pb, traces Fe and P); bronze II shavings in copper bomb (bronze II = 88.0 to 90.0% Cu, 10.0 to 12.0% Sn); cast iron and aluminum shavings with cast iron bomb; cast steel and aluminum shavings with cast steel bomb; aluminum and copper shavings with aluminum bomb; and cast iron, cast steel, aluminum and bronze shavings in cast iron bomb.

Exposures of the trichlorofluoromethane were made with each of the above metals in the presence of 0.12% added moisture and 4% by volume of air, at 150° F. for 108 hours. Decomposition occurred as follows:

Lead sheet	1.99%	Aluminum	0.146%
Bronze I (Cu-Pb-Sn)	2.13%	Bronze II (Cu-Sn)	0.070%
Cast iron	1.56%	Copper	Trace
Cast steel	1.32%		

Lead was most effective in promoting the decomposition of trichlorofluoromethane under these conditions. The lead sheet represented a surface area of approximately only one third that of the Bronze I shavings and yet the amount of decomposition was almost as great. Not only was a considerable amount of lead chloride formed, but the lead sheet completely disintegrated to a mixture of lead pellets and gray lead chloride powder. The presence of lead in the bronze I alloy was likewise accountable for a large amount of decomposition that occurred. Next to lead in effectiveness in promoting the decomposition of trichlorofluoromethane were cast iron and cast steel. These two metals behaved as might be expected, with cast steel being a little less effective than the cast iron. Significantly, the trichlorofluoromethane without any added moisture or air decomposed to a measurable degree in contact with cast steel.

The relative effectiveness of aluminum in contact with moist trichlorofluoromethane was only about one eighth that of cast iron under the same conditions, although Parmelee and Downing (*9*) who tested aluminum and steel in contact with trichlorofluoromethane with 40% added water, report that aluminum was worse than steel.

Copper was the least effective of all metals in promoting decomposition of trichlorofluoromethane. Traces of chloride only were detectable after an exposure of 254 hours. The copper-tin bronze II alloy was almost as ineffective as copper alone, in the presence of moisture and air.

Most of the metals in the combinations in contact with moist trichlorofluoromethane behaved independently for an additive effect in promoting the rate of decomposition, somewhat proportionally to the amount of each present and their relative reactivity. An exception, however, was the combination of copper and aluminum. Both of the metals by themselves had little or no effect upon rates of decomposition of trichlorofluoromethane. In the combination, perhaps because of some electrolytic action between the metals, the rate of decomposition of the moist trichlorofluoromethane was increased more than twofold over that with aluminum alone.

Effect of Metal Surface Area. Most of the stability measurements with moist trichlorofluoromethane were made in presence of a large excess of metal surface present in the form of metal shavings. To determine the effect of the contact area on the rate of decomposition, exposures of the trichlorofluoromethane containing 0.072 weight % added moisture were made in the cast steel bomb using 880 grams of steel shavings in one case, a perforated steel plate of 480 square inch area in another, and no added metal except for the interior surface of the bomb which was 144 square inches; all exposures were made at 150° F. for 108 hours. Decomposition occurred as follows:

Cast steel bomb alone, interior surface of 144 sq. in.	0.185%
Cast steel bomb + perforated steel plate of 480 sq. in., total area of 624 sq. in.	0.48%
Cast steel bomb + 880 grams cast steel shavings, estd. surface area of 1300 sq. in.	0.87%

The amount of decomposition seems to have some definite relation between surface area and the amount of decomposition of trichlorofluoromethane. In the perforated steel sheet and interior surfaces of the bomb, the total area of the former, 624 square inches, was 3.6 times that of the latter and the decomposition was increased 2.6 times. The surface area of the shavings, although not measurable directly, was indicated by the amount of decomposition incurred to be about 1300 square inches.

Effect of Temperature. Exposures of the trichlorofluoromethane were made at 73°, 100°, and 150° F. in the presence of cast steel, and with 0.07 weight % added moisture and 4 volume % air for 108 hours. The results are shown graphically in Figure 4. Even at room temperature (73° F.) appreciable decomposition occurred with a 50% increase at 100° F. and a 300% increase at 150° F.

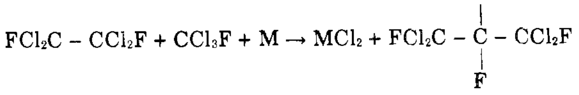
Effect of Exposure Time on Decomposition Rate. This was investigated with cast steel as well as with aluminum, using different amounts of moisture with the two metals (Figure 5). The decomposition attained the maximum rate in the first 30 to 50 hours. Rates gradually decreased at the longer exposure times and tended to become constant. With the higher amount of moisture present in aluminum, the rate of decomposition was almost negligible after 120 hours.

Probable Reaction Mechanism for the Decomposition. There is considerable question concerning the reactions responsible for the decomposition of the trichlorofluoromethane under the conditions of these stability tests. In addition to the inorganic reaction product which was readily detected, there is the organic residue remaining from the hydrolysis of the trichlorofluoromethane which could not be identified, or estimated accurately. Infrared spectrograms of reacted trichlorofluoromethane, both of the vapor and liquid, were compared with spectrograms of pure trichlorofluoromethane without much success. Also, conventional organic analysis methods for the identification of possible reaction products were employed. However, the residual part of the trichlorofluoromethane was not identified. The difficulties encountered in attempts to identify the decomposition product were: The possible reaction products to be expected from the decomposition of the trichlorofluoromethane are not known and have not been described in the literature to date, and the concentrations of these reaction products present in the unreacted trichlorofluoromethane would be of the order of 1 or 2 weight %, much too low for possible detection. To obtain higher concentrations would have required a difficult and efficient low temperature distillation, and their final identification from this concentrated fraction would still be questionable. However, results of the stability studies make it possible to suggest a reaction mechanism for the decomposition of the trichlorofluoromethane.

Three Possible Reactions for the Decomposition. A direct reaction between the trichlorofluoromethane and the metal, resulting in the formation of an ethane derivative

$$2\,CCl_3F + M \rightarrow MCl_2 + FCl_2C - CCl_2F$$

Reactions of this type, such as the Wurtz reaction, are known and it might be that this reaction is catalyzed by the presence of moisture. The reaction does not necessarily produce only ethane derivatives, but molecules of greater chain length might also be formed:



$$FCl_2C - CCl_2F + CCl_3F + M \rightarrow MCl_2 + FCl_2C - \underset{\displaystyle F}{\overset{\displaystyle Cl}{C}} - CCl_2F$$

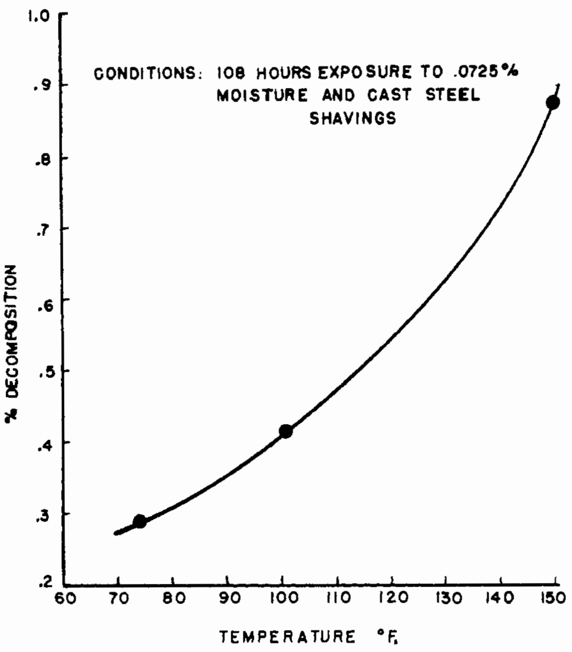


Figure 4. Effect of temperature on the decomposition of trichlorofluoromethane
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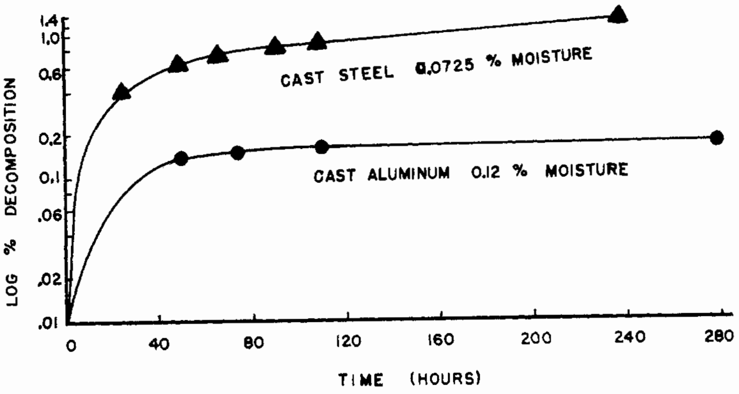
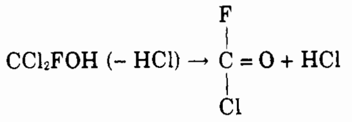


Figure 5. Rate of decomposition of trichlorofluoromethane in the presence of steel vs. aluminum at 150° F.

The trichlorofluoromethane may be decomposed by hydrolysis with the water to form a metallic halide as a secondary reaction between the metal and the hydrogen halide formed

$$CCl_3F + H_2O \rightarrow CCl_2FOH + HCl \qquad (a)$$

with further reaction to form the analog of phosgene by dehydrochlorination


(b)

$$CCl_2FOH\ (-\ HCl) \rightarrow \overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} = O + HCl \qquad (b)$$

An analogous reaction might be that of chloroform formed by the reduction of carbon tetrachloride. In this case the trichlorofluoromethane would be reduced by action of the metal and the water.

$$2\ Cl_3CF + 2H_2O + 2M \rightarrow 2\ Cl_2CFH + MCl_2 + M(OH)_2$$

CONCLUSIONS

An examination of the results of the stability tests with trichlorofluoromethane would seem to favor the interaction between metal and halogenated methane, catalyzed by the presence of moisture, rather than any of the hydrolysis reactions.

Only very slight decomposition occurred in contact with copper, even in the presence of 0.12 weight % moisture. Relatively small amounts of decomposition occurred when in contact with aluminum even after 278 hours and a moisture content of 0.13 weight %. In contact with cast steel and only 0.07 weight % moisture, the chloride by-product formed was almost twice as much as that accounted for on the basis of the water present initially. With cast steel and no added moisture, 0.30% decomposition occurred at 150° F. over 110 hours' exposure.

The steady rate of increase in the decomposition of trichlorofluoromethane with time, following an initial induction period, also supports the view that interaction between trichlorofluoromethane and metal was the predominant. If it were a hydrolysis reaction the rate would have fallen off, with a diminishing concentration of the water, as a result of being consumed as the reactant.

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