

UNCLASSIFIED

AD NUMBER
AD816425
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; 26 MAY 1967. Other requests shall be referred to Naval Research Lab., Washington, DC.
AUTHORITY
NRL ltr, 8 Sep 1969

THIS PAGE IS UNCLASSIFIED

AD816425

Studies of Halogenated Hydrocarbons

Part I--Stability of Fluorocarbons in Air Over Hopcalite Catalyst or Stainless Steel

J. ENOCH JOHNSON

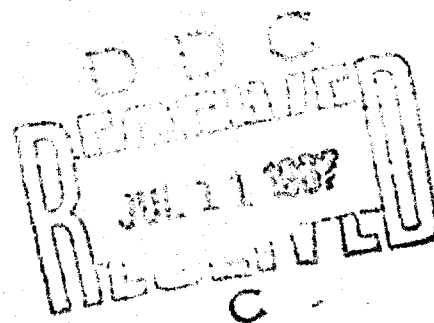
*Fuel Branch
Chemistry Division*

and

JAMES K. MUSICK

*Inorganic and Nuclear Chemistry Branch
Chemistry Division*

May 26, 1967



STATEMENT #2 UNCLASSIFIED

This document is subject to special export controls and each transmittal to a foreign government or foreign nationals may be made only with prior approval.

NAVAL RESEARCH LABORATORY

Washington, D.C.

SEE INSIDE OF COVER FOR DISTRIBUTION RESTRICTIONS

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
EXPERIMENTAL METHOD	1
Apparatus	1
Catalyst	3
Analytical Techniques	3
Significance of Acid Test Results	3
Materials Used	5
EXPOSURE OF CHLOROFLUOROHYDROCARBONS AND SULFUR HEXAFLUORIDE TO HEATED HOPCALITE CATALYST	6
Chlorofluorocarbons Relatively Stable to Hopcalite- Catalyzed Decomposition	6
Chlorofluorocarbons Relatively Unstable to Hopcalite- Catalyzed Decomposition	6
Effect of Lithium Carbonate Added to the Hopcalite Catalyst	8
Effect of Age of Catalyst	9
Effect of Relative Humidity	10
Thermal Stability of Chlorofluorocarbons Exposed to Heated Stainless Steel	10
Sulfur Hexafluoride	11
GENERAL DISCUSSION	11
SUMMARY AND CONCLUSIONS	14
RECOMMENDATIONS	14
ACKNOWLEDGMENTS	14
REFERENCES	15

ABSTRACT

A study was made of the catalytic decomposition of a number of fluorine-containing halogenated hydrocarbons in air, using Hopcalite catalyst in a laboratory-scale reactor which simulates the CO/H₂ burners of nuclear submarines. A few of the highly fluorinated compounds were found to be stable at 305°C. A number of other halogenated hydrocarbons showed substantial decomposition with the production of halogen acids, whereas over stainless steel, a noncatalytic material, very little decomposition occurred. In no case was phosgene observed to be a product. Admixture of lithium carbonate with Hopcalite catalyst had no significant effect on the rate of decomposition of the chlorofluorocarbons. Sulfur hexafluoride in air was stable over Hopcalite at temperatures as high as 425°C.

The results show that use of the chlorofluorocarbons should be as limited as possible in closed environments such as those of nuclear submarines. Where they are needed, as in refrigeration systems, it is recommended that R-114, R-14, or R-12 be used since they show the greatest resistance to Hopcalite-catalyzed decomposition.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problem C08-30
Project SF-013-08-03-4092, 4093, 4094, 4095

Manuscript submitted February 7, 1967.

STUDIES OF HALOGENATED HYDROCARBONS

Part 1 -- Stability of Fluorocarbons in Air Over Hopcalite Catalyst or Stainless Steel

INTRODUCTION

The Navy has a strong interest in the occurrence in nuclear submarine atmospheres of the vapors of certain halogenated hydrocarbons (halocarbons), especially those used in the refrigeration systems. A major concern has been the corrosive effects of acidic decomposition products of these compounds, particularly from the CO/H₂ burner. Laboratory and shipboard studies of the effects of these corrosive effluents upon the construction materials in the burner itself and upon other shipboard equipment are discussed in Ref. 1.

Chlorofluorocarbons, which include the common refrigerants, generally are not very reactive at ordinary temperatures. This inertness, plus good solvent power, has led to increasing use of these compounds as refrigerants, aerosol propellents, degreasers, fire extinguishing agents, and general solvents. However, these compounds will react with metals, water, and other chemicals, particularly at higher temperatures. A review of the reactions of chlorofluorocarbons with metals has been published recently (2). This reference is concerned primarily with reactions between the metals and the liquid or vapor forms of these compounds in closed systems in the absence of other compounds. The most reactive metal studied was aluminum, and the least reactive was stainless steel. Hama and Curley (3), however, give information concerning the breakdown of chlorofluorocarbons in combustion equipment. This decomposition leads to severe corrosion of metal parts, even at low concentrations of the halocarbons. Metal chloride and fluoride salts have been found similarly in the corrosion products from submarines by analysis at NRL (1,4).

As part of a continuing study at NRL of organic contaminants in nuclear submarine atmospheres, the stability over Hopcalite catalyst of a number of types of compounds has been investigated in a simulated burner (4,5). Included in this work were detailed studies of a few halogenated hydrocarbons. The decomposition of these compounds in air when passed over Hopcalite catalyst at 315°C ranged from slight in the case of CCl₂F₂, R-12, to virtually complete with CH₃CCl₃, methyl chloroform.

As a result of renewed interest, additional chlorofluorocarbons have been studied recently in the bench-scale Hopcalite burner and are included in the present report. In addition, some data are included concerning the thermal stability of several of these compounds when the Hopcalite was replaced by a noncatalytic material, in this case stainless steel. Although not a halogenated hydrocarbon, sulfur hexafluoride was included as a matter of collateral interest.

EXPERIMENTAL METHOD

Apparatus

The apparatus used in all these experiments was varied slightly to suit the special case but was essentially similar to the one described in an earlier report (4) and shown

schematically in Fig. 1. This laboratory reactor unit was built to simulate the conditions of shipboard catalytic combustion units in regard to flow rate, residence time, and temperature. The reactor was essentially a 28-inch length of 1-1/8-inch-I.D. stainless steel tubing, mounted vertically and suitably lagged. Stainless steel turnings filled the 12-inch lower section, which was heated by Nichrome windings. A variable transformer was used to control the temperature of the air entering the 5-inch catalyst bed, which was supported on a circular section of stainless steel screen. A space velocity of 21,000 hr^{-1} was obtained with an air flow of 1 cfm and was used for all experiments except as noted. A chromel-alumel thermocouple was located on the inlet side of the catalyst and connected to a meter which indicated the temperature. Although this temperature was recorded as the burner temperature, an additional thermocouple sometimes was placed in the well downstream of the catalyst to measure the temperature drop through the bed. At 425°C the temperature drop was about 55°C; at 375°C, the drop was 40°C. The controlled heater permitted the burner to be operated over a wide range of selected constant temperatures.

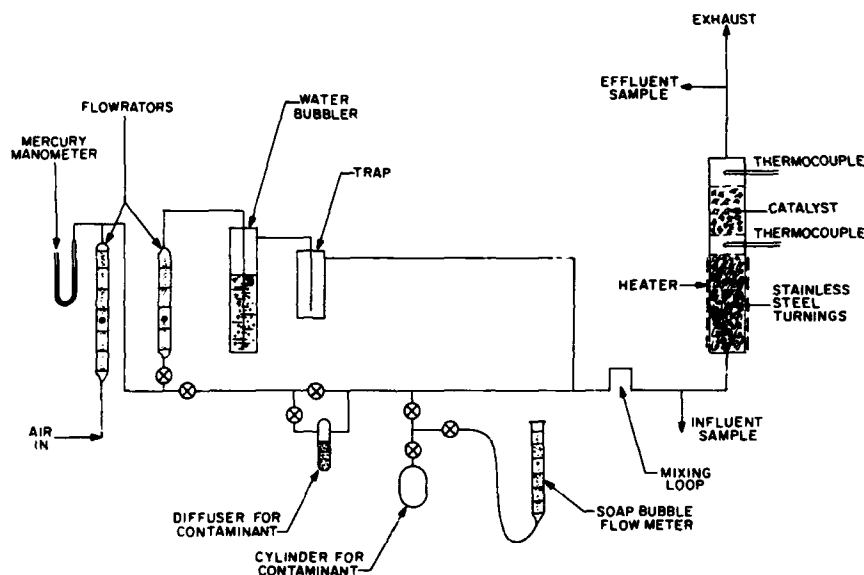


Fig. 1 - Schematic diagram of bench-scale catalytic combustor

The apparatus (Fig. 1) included a water bubbler through which any proportion of the dry inlet air could be passed. By this means the relative humidity of the air could be controlled in the range of 10% to 90% at room temperature. The halogenated hydrocarbons were introduced into the air stream by several means. The contaminant had to be added at a constant rate throughout a test period to achieve a steady state of operation and meaningful results. Gaseous contaminants were fed into the air stream from steel bottles under their own vapor pressure at a rate controlled by a fine needle valve. Liquid contaminants were added to the air stream by diverting a portion of the dry air through a diffuser kept in a simple constant-temperature bath. The concentration of the liquid contaminant was controlled by the temperature of the diffuser and by the proportion of air passed through the diffuser. Because of the low concentrations of chlorofluorocarbons

used, it was necessary to avoid rubber and plastic materials of construction. Only metal and glass were used downstream of the point of introduction of the organic compounds.

Catalyst

The Hopcalite catalyst was manufactured by Mine Safety Appliances Corp. and obtained through Navy supply channels. It was purchased on the military specification, Mil-C-21665 (Ships), 12 December 1956, amended 11 May 1959. Chemical analyses showed 78.3% MnO_2 , 13.1% CuO , and loss on ignition 7.9%, presumably water or chemisorbed gases. The catalyst, about 6-mesh size, had an apparent density of 1.0 g/cm^3 . In experiments to determine the innate thermal instabilities of the chlorofluorocarbons the catalyst was replaced by 19 Cr-8Ni stainless steel pellets in the form of 4-40 machine screw nuts used because of their availability.

Analytical Techniques

Gas chromatography was used to determine the concentration in air of the halogenated hydrocarbon being studied. The difference between the concentration of compound in the effluent air and that in the influent air was a measure of the amount of compound destroyed in the burner. A Beckman Model GC2a gas chromatograph was used in all cases. The chromatograph was calibrated by using air samples containing the contaminants in a known concentration in the desired range. These standards were prepared by injecting the calculated volumes of liquid or vapor into evacuated stainless steel bottles, followed by pressurizing with air to appropriate levels. Table 1 contains details of the chromatographic equipment and conditions used as well as retention times for the halocarbons used. The limits of error for quantitative data, which were usually based on peak height, were about $\pm 3\%$.

The acid content of the burner effluent was estimated by using the NRL Acid Vapor Detector, a device for exposing a detector paper (6). Blank tests were also made, comprising measurements of the acid content of the effluent with no contaminant entering the burner and the influent with contaminant. The concentrations of acid found in the effluent were corrected on the basis of the blank tests. These corrected values were used to help determine the degree of breakdown of the compounds in the burner.

The burner effluent was tested for chlorine and phosgene content with appropriate detector tubes, obtained from Mine Safety Appliances Corporation and Draegerwerke, respectively. The relative humidity of the burner influent was determined when necessary by means of Draeger detector tubes.

Significance of Acid Test Results

Although it was known (4,5) that Hopcalite catalyst would retain as halides a substantial amount of the halogen acids produced during the decomposition of the halocarbons, the use of the acid detector paper in the effluent was nevertheless helpful in detecting low levels of decomposition. The effectiveness of this technique over gas chromatography at low levels of decomposition is based on the greater ease of seeing a small amount of a new substance, the acid, as opposed to detecting a small difference between two large numbers, i.e., a slight loss of halocarbon. In practice, a trace of acid in the burner effluent often indicated a slight decomposition, not detectable by the gas chromatograph measurements, of halocarbon concentrations.

Used catalyst gave off acid when the burner was at the temperature and air flow conditions for a run but with no contaminant in the entering air stream. These acid-retention

Table 1
Details of Gas Chromatographic Procedures Used for Quantitative Analysis
of Halogenated Compounds

Compound	Column*				Detector	Corrected Retention Time (min)
	Length (ft)	Support	Liquid Phase	Temp (°C)		
R-14	8	60-80 mesh A.S.L. silica gel	None	40	T.C.,† 300 ma	0.2
R-C318	6	50-80 mesh Porapak Q	None	130	Hydrogen flame	3.6
R-114	12	Chromosorb P	15% DC 550 Silicone	40	Hydrogen flame	0.5
R-12	12	Chromosorb P	15% DC 550 Silicone	40	Hydrogen flame	0.4
R-11	12	Chromosorb P	15% DC 550 Silicone	40	Hydrogen flame	2.0
R-21	12	Chromosorb P	15% DC 550 Silicone	40	Hydrogen flame	1.8
R-22	12	Chromosorb P	15% DC 550 Silicone	40	Hydrogen flame	0.2
R-113	12	Chromosorb P	15% DC 550 Silicone	70	Hydrogen flame	1.15
R-133a	8	Gaschrom R	15% PEG-400	70	Hydrogen flame	1.10
R-216ac	8	Gaschrom R	15% PEG-400	40	Hydrogen flame	0.60
R-216ab	8	Gaschrom R	15% PEG-400	40	Hydrogen flame	0.65
Sulfur hexafluoride	6	50-80 mesh Porapak Q	None	70	T.C.,† 300 ma	1.0

*All columns were made of 1/4-inch copper or stainless steel tubing.

†Thermal conductivity detector. The T.C. detector was protected by venting the column effluent until the air peak had passed.

characteristics of the Hopcalite made it necessary to correct acid determinations by blank test results.

Because of the retention of acid on the catalyst, no quantitative significance is placed on the acid values. In order to facilitate analyses for acid gases no lithium carbonate was mixed with the Hopcalite in most of the studies.

Materials Used

The structural formula, boiling point, and source of the halogenated hydrocarbons used are given in Table 2. All compounds were 99 mol-% pure or better, based on manufacturer's statements.

The sulfur hexafluoride used was obtained from Allied Chemical Co., General Chemical Division, via the Naval Ordnance Laboratory. No interfering impurities, including no SO_2F_2 , SO_2 , or SF_4 , were detected in this sample by gas chromatography.

Table 2
Halogenated Compounds Studied

Chlorofluoro-carbon	Structural Formula	Boiling Point (°C)	Source	Commercial Uses
R-14	CF_4	-128.0	Dupont*	Refrigerant, aerospace propellant
R-C318	C, F, cyclic	-6.0	Dupont*	Heat transfer agent, good propellant
R-114	$\text{CClF}_2\text{-CClF}_2$	3.8	Dupont*	Blowing agent, refrigerant, propellant
R-12	CCl_2F_2	-29.8	Allied†	Refrigerant, dielectric gas, propellant
R-11	CCl_3F	23.8	Dupont*	Blowing agent, solvent, refrigerant, aerosol propellant
R-21	CHCl_2F	8.9	Dupont*	Refrigerant, propellant, solvent
R-22	CHClF_2	-40.8	Dupont*	Low temperature solvent, refrigerant, blowing agent, propellant
R-113	$\text{CClF}_2\text{-CCl}_2\text{F}$	47.5	Dupont*	Refrigerant, solvent, dry cleaning agent, blowing agent
R-133a	$\text{CF}_3\text{-CH}_2\text{Cl}$	—	Allied†	Experimental
R-216ac	$\text{CClF}_2\text{-CF}_2\text{-CClF}_2$	35.0	Union Carbide Co.	Experimental
R-216ab	$\text{CClF}_2\text{-CClF-CF}_3$	34.5	Dupont*	Experimental
R-114B2	$\text{CBrF}_2\text{-CBrF}_2$	47.5	Dupont*	Refrigerant

*E. I. du Pont de Nemours and Co., Inc.

†General Chemical Division, Allied Chemical Co.

EXPOSURE OF CHLOROFLUOROHYDROCARBONS AND SULFUR HEXAFLUORIDE TO HEATED HOPCALITE CATALYST

A number of chlorofluorohydrocarbons were exposed to Hopcalite under conditions which simulate the operation of a nuclear-submarine type of CO/H₂ catalytic burner. Air containing the halogen compounds was passed through a bed of the catalyst, and evidences of decomposition were noted. On the basis of the results the compounds studied fell naturally into two general groups: relatively stable and relatively unstable. Although such a separation into two groups is arbitrary, it does facilitate the discussion of results.

Chlorofluorocarbons Relatively Stable to Hopcalite- Catalyzed Decomposition

Table 3 contains a summary of the extent of decomposition of the relatively stable chlorofluorocarbons. It should be noted that no detectable loss was observed with any of the six compounds listed here on passage through the Hopcalite bed at temperatures as high as 305°C. In a few cases measurable loss of the halocarbon was evident at 360°C. The detection of acid in the effluent is a more sensitive evidence of incipient decomposition. Up to a few ppm of acid could be detected from all of the compounds when passed over Hopcalite heated to 415°C, but the more stable ones yielded only a trace. However, the acid values were counted as indications only, because it is known that some of the acid which is developed is held up by the Hopcalite catalyst.

Table 3
Chlorofluorocarbons Which Are Resistant to Hopcalite-Catalyzed Decomposition

Compound	Structural Formula	Vapor Conc. in Air (ppm)	Loss of Compound* (%)			Acid Detected† (ppm)		
			305°C	360°C	415°C	305°C	360°C	415°C
R-14	CF ₄	285	—†	—	0	—	—	1-2
R-12	CCl ₂ F ₂	420-440	0	0	6	trace	1-2	5
R-C318	Cyclic C ₄ F ₈	85	0	—	0	0	—	1
R-114	CClF ₂ -CClF ₂	85-410	—	0	0	—	trace	trace
R-216ac	CClF ₂ -CF ₂ -CClF ₂	30-100	0	<1	—	trace	1	—
R-216ab	CF ₃ -CClF-CClF ₂	30-100	0	2	—	2	3	—

*Concentration of halogen compound determined by gas chromatography.

†Acid detected by NRL Strong Acid Detector paper (Ref. 6).

‡A dash indicates that the experiment under question was not performed.

No free chlorine or phosgene was detected in the burner effluents of these compounds. The limit of detection of these potential products was estimated to be about 0.1 ppm.

Chlorofluorocarbons Relatively Unstable to Hopcalite- Catalyzed Decomposition

The data for those chlorofluorocarbons found to decompose fairly readily when passed through a bed of Hopcalite at elevated temperatures are summarized in Table 4.

Table 4
Halogenated Compounds Which Are Susceptible
to Hopcalite-Catalyzed Decomposition

Compound	Structural Formula	Vapor Conc. in Air (ppm)	Loss of Compound* (%)			Acid Detected† (ppm)		
			305°C	360°C	415°C	305°C	360°C	415°C
R-11	CCl_3F	30-100	17	37	—†	5	10	—
R-21	CHCl_2F	100	17	37	—	—	—	—
R-22	CHClF_2	100	22	41	48	2-4	5-10	10-25
R-113	$\text{CClF}_2 - \text{CCl}_2\text{F}$	10	1.5	5	26	trace	—	2.5
R-133a	$\text{CF}_3 - \text{CH}_2\text{Cl}$	100	23	47	—	10	20	—
R-114B2 §	$\text{CBrF}_2 - \text{CBrF}_2$	100	30	—	—	—	—	—

*Concentration of the halogen compound was determined by gas chromatography.

†Acid was detected by NRL Strong Acid Detector paper (Ref. 6).

‡A dash indicates that the experiment under question was not performed.

§Data for this compound was taken from Refs. 4 and 5.

A substantial percentage of all of these compounds decomposed when passed through a bed of Hopcalite heated to 305°C. Although data were not taken for all cases, significant amounts of acid were detected in the burner effluent of these compounds, as expected. Here again, due to hold-up in the catalyst bed, the acid yield should not be taken as quantitative evidence. However, the loss of halocarbon which is based on gas chromatographic analyses is quantitative and reproducible.

No phosgene was detected in the burner effluents of any of these compounds. The limit of detection was estimated to be 0.1 ppm. No free chlorine was detected in any case except with R-133a. At 360°C, about 2 ppm of chlorine were found. In a few cases, e.g., R-11 and R-21, the appearance of very small chromatographic peaks, denoting possible organic products, was observed. These peaks were not identified further at this time.

More detailed data were obtained for three compounds, R-113, R-21, and R-22, and given the Arrhenius treatment as shown in Fig. 2. The log of percent decomposition of these compounds, as plotted against the reciprocal of absolute temperature, is reasonably linear. According to Bond (7), the rates of heterogeneous reactions generally conform reasonably well to the Arrhenius equation. The activation energies which are calculated from the Arrhenius plot, however, are not considered to be true activation energies but are generally referred to as apparent activation energies. Each of the latter is lower than the true activation energy by the heat of adsorption. It is generally held that the type of adsorption which is effective in surface catalysis is chemisorption or activated adsorption (7,8). Chemisorption tends to cause a partial relaxation or loosening of the bonds in the adsorbed molecules, making reaction easier to attain by requiring less energy to form the activated complex for the reaction. Thus it is not unexpected that the activation energy for a surface-catalyzed reaction has been found to be less than for the corresponding homogeneous reaction. It is generally agreed that it is the decrease in this energy of activation that allows the greatly increased rates of catalyzed reactions.

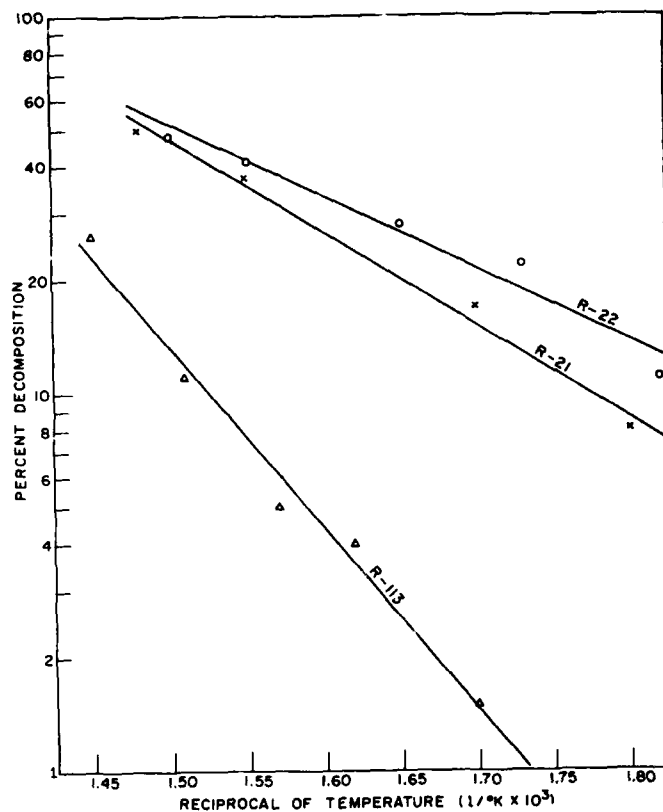


Fig. 2 - Percent decomposition of R-113, R-21, and R-22 versus the reciprocal of absolute temperature

Although the activation energy calculated from the Arrhenius plots such as given in Fig. 2 is an apparent activation energy E_a , it is of interest to make these calculations for the compounds shown in Fig. 2 so that comparisons can be made with known activation energies of other catalyzed and noncatalyzed reactions. The apparent activation energies calculated for R-21 and R-22 are 11.7 and 8.9 kcal/mol, respectively. For R-113, the calculated value for E_a is 21.9 kcal/mol.

Effect of Lithium Carbonate Added to the Hopcalite Catalyst

Laboratory studies (1) showed that a particularly effective way to control the acid halides which are formed in the CO/H₂ burner is to mix lithium hydroxide with the Hopcalite before placing it in the catalyst bed. The effectiveness of this treatment has been confirmed by shipboard tests. Subsequently, the intermixing of 10-vol-% lithium hydroxide with the Hopcalite has become standard shipboard procedure. Within a short time the lithium hydroxide in the burners is converted to lithium carbonate because of the high carbon dioxide content of the ship's atmosphere. For ease of handling, the lithium hydroxide may be converted to lithium carbonate before mixing with the Hopcalite.

This may be done by exposing the hydroxide to ship's atmosphere in the canisters which serve for emergency removal of carbon dioxide.

There was some question as to whether the presence of lithium carbonate in the Hopcalite bed might tend to accentuate the decomposition of halocarbons at a given temperature. During this study, most runs were made without the lithium carbonate, the absence of which facilitates the detection of incipient decomposition of the halogen compounds. However, several runs were made with 10-vol-% lithium carbonate present to learn if there was enhanced decomposition. This was done mostly in cases of compounds which were found to be relatively stable over Hopcalite at 305°C or higher.

The compounds, R-114, R-216ab, and R-11, were passed through the burner at 305°C and 360°C with Hopcalite alone and then with mixed Hopcalite/lithium carbonate. The results are given in Table 5. The conclusion derived from these data is that the presence of lithium carbonate in the Hopcalite catalyst did not influence the rate of decomposition of these halocarbons. The effectiveness of the lithium carbonate in removing halogen acids from the effluent air stream is demonstrated by the almost complete absence of acid in these cases. This result is shown most clearly in the case of R-11, where the added lithium carbonate dropped the acid in the effluent to 0-1 ppm from 5-10 ppm without the carbonate. A much more detailed study of the effectiveness of various acid scrubbers has been published recently (9).

Table 5
Effect of Added Lithium Carbonate on Hopcalite-Catalyzed Decomposition

Compound	Loss of Compound (%)		Acid Detected (ppm)	
	305°C	360°C	305°C	360°C
Hopcalite Alone				
R-114	0	0	0	trace
R-216ab	0	2	2	3
R-11	17	37	5	10
Hopcalite plus 10-vol-% Lithium Carbonate				
R-114	0	0	0	0
R-216ab	0	0	0	0
R-11	17	35	trace	1

Effect of Age of Catalyst

In previous work (4) with the halo hydrocarbons and Hopcalite, it was observed that fresh catalyst was more active in promoting decomposition of halogenated compounds. For example, during an 8-hour run using a fresh charge of Hopcalite, the decomposition of R-114B2 fell from 30% to about 5%. In the case of methyl chloroform, CH_3CCl_3 , the extent of decomposition dropped from 50% to 32% during 6-1/2 hours.

In the present work, a run was made with R-114 at 8% R.H. and 360°C, starting with a fresh batch of catalyst. During the second hour of use, the gas chromatograph indicated

6% breakdown, although no acid could be detected in the effluent. After 8 hours, the chromatograph showed no decomposition of R-114, although a definite trace of acid was detected in the burner effluent. The fresh catalyst was more efficient in both breaking down the R-114 and in retaining the acid produced. Analyses performed during earlier studies (4) showed substantial retention of halides by the catalyst.

The catalyst in the bench-scale burner was used for many hours in successive tests in order to more nearly simulate the conditions of the shipboard burners. The freshest catalyst used in getting the data for this report (unless otherwise noted) had had about 8 hours usage.

Effect of Relative Humidity

Runs made with R-114 and R-12 showed no variance in degree of decomposition over Hopcalite whether the air entering the burner was at 68% or 88% R.H. No significant effect was observed in decomposition of R-11 at 50% or 68% R.H. As shown in Table 7, no significant difference was noted in the stability of SF_6 at 8% or 71% R.H. To avoid repetitive runs, most of them were made at about 68% R.H., because it was felt that should any effect of water content occur, it would likely be more severe at higher R.H.

Thermal Stability of Chlorofluorocarbons Exposed to Heated Stainless Steel

Five chlorofluorocarbons, R-11, R-12, R-21, R-22, and R-114 were exposed to stainless steel pellets under the same flow conditions used with Hopcalite catalyst. In a study (2) of the reactivity of a number of halohydrocarbons with metals it was concluded that the least reactive metal studied was stainless steel. Therefore, this metal was chosen for the present study to represent, as nearly as possible, a noncatalytic material in contrast to Hopcalite catalyst. With stainless steel it was hoped to approximate the innate thermal stability of the halogen compounds. The results are given in Table 6. It can be seen that R-114 and R-12 showed no sign of decomposition over stainless steel even at 415°C. By comparison, R-114 was also very stable over Hopcalite, even at 415°C, but R-12 showed 6% loss by gas chromatography at 415°C. (See Table 3.)

Table 6
Stability of Chlorofluorocarbons Exposed to Stainless Steel

Compound	Vapor Conc. in Air (ppm)	Loss of Compound (%)		Acid Detected (ppm)	
		360°C	415°C	360°C	415°C
R-114	100	—	0	—	0
R-12	720	—	0	—	0
R-11	200	—	0	—	trace
R-21	100	0	4	0	1-2
R-22	100	0	0	0	trace

R-11 and R-22 were only slightly decomposed over stainless steel. R-21 was somewhat less stable at 415°C but showed no decomposition at 360°C. All three compounds were considerably decomposed over Hopcalite; e.g., as seen in Table 4, about 20% was destroyed in each case at 305°C. These data show the strong catalytic effect of Hopcalite in promoting the decomposition of these halogenated hydrocarbons. Conversely, it demonstrates the excellent thermal stability of the halo hydrocarbons in the presence of stainless steel.

Sulfur Hexafluoride

Air containing about 500 ppm of sulfur hexafluoride, SF_6 , entered the reactor containing Hopcalite in the catalyst bed. Three runs of 3-4 hours duration each were made as outlined in Table 7. The two runs at 425°C with air of low and high relative humidity are extremes in the range of water vapor concentrations which might be expected in practice. There was no evidence of breakdown of SF_6 even at 425°C based on gas chromatographic analyses. The variations in influent and effluent concentrations during a given run as shown in Table 7 are within the limits of accuracy of the method. No additional chromatographic peaks were noted. At 425°C there was a positive indication of only about 1 ppm of acid in the effluent; at 315°C no acid was noted. It was concluded, therefore, that SF_6 would be stable in presence of Hopcalite catalyst under the present operating conditions of the CO/H_2 burner ($600^\circ \pm 25^\circ \text{F}$) in a nuclear submarine.

Table 7
Stability of Sulfur Hexafluoride in Contact with Hopcalite

Run No.	Duration (Hr.)	Catalyst Temp. (°C)	Moisture Content of Air (Calc: as R.H. at 72°F)	Concentration of SF_6 in Air (ppm)	
				Influent	Effluent
1	3.5	315	8	495	500
2	3.75	425	8	473	464
3	3.25	425	71	486	486

GENERAL DISCUSSION

The present work has demonstrated a pronounced catalytic effect toward the decomposition of chlorofluorocarbons by Hopcalite as compared with stainless steel. These results confirm some brief observations made earlier at NRL (4). Eiseman (2) had found that stainless steel is, among the metals, one of the least effective in promoting the decomposition of chlorofluorocarbons. Also data given by Norton (10) shows that metal oxides generally have a pronounced catalytic effect toward pyrolysis of "Freons," which are chlorofluorocarbon compounds. Practically all published work of this sort was obtained from studies toward the application of these compounds to refrigeration systems, and the results argue for keeping impurities such as water and oxygen out of such systems. The interest in the present study, on the other hand, concerns the stability of chlorofluorocarbons in air, and in the presence of water vapor, carbon dioxide, and other impurities. Very little applicable information was found in the literature concerning low concentrations of chlorofluorocarbons in air.

According to Ref. 11, the thermal stability of chlorofluorocarbons in the form of liquid or concentrated vapor is markedly dependent on the nature of the other materials that are present. These "other materials" may include surfaces, gases, and vapors

(such as water vapor). The true pyrolytic behavior of the halocarbon in the absence of other gases and vapors is very difficult to determine, because even traces of impurities may have important effects. As illustration of this, some data given in Ref. 11 for halocarbon compounds passed through a heated quartz tube are summarized in Table 8. On the basis of the temperature at which the first trace of acid was detected, R-11 would appear to be the most stable compound in the group of five, which includes R-114 and R-12. Based on free halogen, R-114 and R-12 were more stable. It is surmised by the authors that the appearance of acid is due to slight impurities containing hydrogen, such as other organic compounds or water, but that the free halogen is a true indication of the pyrolysis of the compound.

Table 8
Pyrolysis in a Quartz Tube*

Compound	Structural Formula	Temperature for First Trace of Decomposition			
		Acid		Halogen	
		°F	°C	°F	°C
Freon-114	$\text{CClF}_2\text{-CClF}_2$	700	371	940	504
Freon-12	CCl_2F_2	700	371	1000	538
Freon-11	CCl_3F	780	416	840	449
Freon-22	CHClF_2	550	288	900	482
Freon-113	$\text{CCl}_2\text{F-CClF}_2$	570	299	570	299

*Adapted from data given in Ref. 11.

The general conclusion that results from the study of data given in previous publications (2, 10-12) is that no overall listing of these compounds in order of increasing thermal stability is valid for all situations because of the strong influence of the environment, including heterogeneous factors such as catalysts, and homogeneous ones such as other gases and vapors. The need becomes obvious for the experimental determination of the stability of each candidate compound in an environment simulating operating conditions as closely as practicable.

Based on the previous discussion it follows that in the consideration of halocarbon refrigerants for use in the nuclear submarine environment the most important stability factor is the rate of decomposition in the CO/H_2 burner. In the present study, consequently, thermal stability data were obtained in a catalytic reactor which, although bench-scale, simulated the CO/H_2 burner of an operating submarine in regard to bed depth and space velocity (a term which may be considered to mean the reciprocal of contact time).

The potent catalytic activity of the Hopcalite which is used in the CO/H_2 burner is shown by comparing the data in Table 6 including stainless steel with the data in Tables 3 and 4 involving Hopcalite. For example, R-22, which lost 22% at 305°C over Hopcalite, showed barely a trace of decomposition at 415°C over stainless steel. In this connection, Norton (10) studied the decomposition of R-22 on silica in the range of 425° to 525°C and found an activation energy of 49 kcal/mole. This value compares well with 55.6 kcal/mole obtained by Edwards and Small (13) for the decomposition of R-22 by itself in a

platinum vessel at 533° to 750°C. They found that below 550°C the decomposition reaction in platinum is quite slow. These literature data are in contrast with the present work, in which the decomposition of R-22 over Hopcalite was found to be rapid even at 305°C, with a calculated activation energy of 8.9 kcal/mole.

The presence of such toxic compounds as phosgene and chlorine in the decomposition products of halocarbons has been noted in the literature. Chlorine has been observed under various conditions (11). Phosgene has been reported on occasion also. For example, Ref. 14 notes that phosgene is an intermediate product formed from the partial decomposition of "Freon-12" in a flame. It is also stated, however, that when the molecule begins to decompose it nearly always goes all the way, so that the amounts of acid formed are greater than the amount of phosgene formed. Consequently, in the present studies, sensitive methods of detection were used to look for both chlorine and phosgene.

The absence of phosgene in the effluents of any of the Hopcalite-catalyzed decompositions of chlorofluorocarbons studied is gratifying. Also in only one case, R-133a, was free chlorine detected. This is noteworthy because, for all the compounds listed in Table 8, free halogen was observed upon pyrolysis in quartz at somewhat higher temperatures. The absence of these two toxic compounds, phosgene and chlorine, is obviously important to the habitability of nuclear submarine atmospheres.

Several specific observations concerning the relative stabilities of the fluorocarbons over heated Hopcalite become apparent when the data of Tables 3 and 4 are examined. These are summarized as follows:

- (i) The fully fluorinated compounds are very stable, e.g., CF_4 and C_4F_8 .
- (ii) Increasing the number of Cl atoms in the molecule decreases the stability. This is shown by the methane series in which the relative stabilities are $\text{CF}_4 > \text{CCl}_2\text{F}_2 \gg \text{CCl}_3\text{F}$. Also $\text{CClF}_2 - \text{CClF}_2 > \text{CCl}_2\text{F} - \text{CClF}_2$.
- (iii) Substitution of a hydrogen atom markedly decreases the stability of the molecule. For example, $\text{CCl}_2\text{F}_2 \gg \text{CHClF}_2$. It is interesting to note that $\text{CF}_3 - \text{CH}_2\text{Cl}$ is a relatively unstable compound also.
- (iv) The replacement of the Cl atoms in the very stable R-114, $\text{CClF}_2 - \text{CClF}_2$, by bromine atoms yields R-114B2, $\text{CBrF}_2 - \text{CBrF}_2$, a very unstable compound relative to the fully fluorinated compounds.

In regard to the repeatability of these stability experiments, it is of interest that the amount of water vapor present within reasonable limits did not appear to be a significant factor. This fact is probably due to the overriding factor represented by the catalyst. Once a sufficient minimum supply of water in the atmosphere is achieved, the addition of more water molecules apparently is unimpressive. The loss of activity of fresh catalyst in the presence of halocarbons is not easy to explain. It suggests that some very active sites are present which are nullified quickly, resulting in decreased effectiveness in decomposition of halocarbon. The catalyst seems to reach an intermediate stable state, however. That the Hopcalite is very resistant to complete deactivation is shown also by the long-term effectiveness in the oxidation of carbon monoxide by shipboard installations of Hopcalite even in the presence of continuously significant concentrations of halocarbons. In contrast to this is the general evidence (15) that supported palladium catalysts are susceptible to poisoning by halogen compounds such as R-12.

SUMMARY AND CONCLUSIONS

1. These studies have shown Hopcalite to be a strong catalyst toward promoting the decomposition of chlorofluorocarbons in a flowing air stream.
2. A number of the chlorofluorocarbons likely to be present in submarines were relatively unstable in contact with Hopcalite at temperatures as low as 305°C (580°F). These compounds would be expected to decompose profusely in the CO/H₂ burner of nuclear submarines, which is operated at 315°C (600°F), with copious yields of halogen acids.
3. Several of these chlorofluorocarbons were found to be quite stable in air passed over Hopcalite at 305°C. A few showed only slight decomposition at 415°C.
4. The admixture of lithium carbonate with Hopcalite catalyst did not accentuate the decomposition of the chlorofluorocarbons.
5. Sulfur hexafluoride was stable in an air stream passed over Hopcalite catalyst at temperatures as high as 425°C.

RECOMMENDATIONS

In view of the tendency of many chlorofluorocarbon compounds to decompose in the Hopcalite burner to yield corrosive acids, it is recommended again that no unnecessary use be made of these compounds aboard nuclear submarines.

In situations where chlorofluorocarbons must be used, e.g., in refrigeration systems, the experimental information summarized here concerning the stability of these compounds to Hopcalite should be used in order to permit the selection of those which would be the least troublesome aboard ship.

In light of the stability data given in this report, it is recommended that R-114, R-14, or R-12 be used in refrigeration systems planned for closed environments such as submarines where the refrigerant vapors may be passed through a catalytic burner containing Hopcalite. The choice of a given refrigerant must also depend on information available from the manufacturers concerning its suitability for the intended application.

ACKNOWLEDGMENTS

The authors are indebted to Dr. Merle Umstead and Dr. Fred Williams of the Fuels Branch, Chemistry Division for advice and assistance in developing the gas chromatographic procedures used.

REFERENCES

1. Thomas, F.S., Ch. 7 of "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," Miller, R.R., and Piatt, V.R., eds., NRL Report 5465, Apr. 21, 1960
2. Eiseman, B.J., Jr., "Reactions of Chlorofluorohydrocarbons with Metals," ASHRAE J. 5:63 (1963)
3. Hama, G.M., and Curley, L.C., "Corrosion of Combustion Equipment by Chlorinated Hydrocarbon Vapors," Air Engineering, Apr. 1965
4. Christian, J.G., and Johnson, J.E., "Catalytic Combustion of Nuclear Submarine Atmospheric Contaminants," NRL Report 6040, Mar. 20, 1964
5. Christian, J.G., and Johnson, J.E., "Catalytic Combustion of Atmospheric Contaminants over Hopcalite," Intern. J. Air Water Pollution 9:1 (1965)
6. Williams, D.D., Johnson, E.T., and Miller, R.R., "A Method for the Determination of Strong-Acid Vapors in the PPM Range," NRL Report 6332, Oct. 14, 1965
7. Bond, G.C., "Catalysis by Metals," New York: Academic Press, 1962, p. 125
8. Glasstone, S., and Lewis, D., "Elements of Physical Chemistry," 2nd ed., Princeton: Van Nostrand, p. 650, 1960
9. Gadomski, S.T., "Dry-Packed Beds for the Removal of Strong-Acid Gases from Recycled Atmospheres," NRL Report 6399, Aug. 1966
10. Norton, F.G., Refrigeration Engineering 65:33 (1957)
11. "Thermal Stability of the "Freon" Compounds," Technical Bulletin B-33, Freon Products Division, E.I. du Pont de Nemours and Co., Inc., Wilmington, Delaware
12. "Properties and Applications of the "Freon" Fluorocarbons," Technical Bulletin B-2, Freon Products Division, E.I. du Pont de Nemours and Co., Inc., Wilmington, Delaware, 1964
13. Edwards, J.W., and Small, P.A., "Kinetics of the Pyrolysis of Chlorodifluoromethane," Ind. Eng. Chem., Fundamentals 4:396 (1965)
14. "Decomposition of "Freon-12" Refrigerant," Bulletin S-20, Freon Products Division, E.I. du Pont de Nemours and Co., Inc., Wilmington, Delaware, Mar. 23, 1961
15. Johns, R.H., "Kinetics and Catalyst Selection in the Combustion of Atmospheric Trace Contaminants," Chemical Engineering Progress Symposium Series, 62:81 (1966)

<p style="text-align: center;">UNCLASSIFIED</p> <p>Naval Research Laboratory. Report 6546. STUDIES OF HALOGENATED HYDROCARBONS. Part 1 - Stability of Fluorocarbons in Air Over Hopcalite Catalyst or Stainless Steel, by J. Enoch Johnson and James K. Musick. 20 pp. and figs., May 26, 1967</p> <p>A study was made of the catalytic decomposition of a number of fluorine-containing halogenated hydrocarbons in air, using Hopcalite catalyst in a laboratory-scale reactor which simulates the CO/H₂ burners of nuclear submarines. A few of the highly fluorinated compounds were found to be stable at 305°C. A number of other halogenated hydrocarbons showed substantial decomposition with the production of halogen acids, whereas over stainless steel, a noncatalytic material, very little decomposition occurred. In no case was phosgene observed to be a product. Admixture of</p> <p style="text-align: right;">UNCLASSIFIED (over)</p>	<ol style="list-style-type: none"> 1. Nuclear submarines - Equipment 2. Fluorocarbons - Decomposition 3. Hopcalite - Catalytic properties <p style="text-align: right;">I. Johnson, J. E. II. Musick, J. K.</p>	<ol style="list-style-type: none"> 1. Nuclear submarines - Equipment 2. Fluorocarbons - Decomposition 3. Hopcalite - Catalytic properties <p style="text-align: right;">I. Johnson, J. E. II. Musick, J. K.</p>
<p style="text-align: center;">UNCLASSIFIED</p> <p>Naval Research Laboratory. Report 6546. STUDIES OF HALOGENATED HYDROCARBONS. Part 1 - Stability of Fluorocarbons in Air Over Hopcalite Catalyst or Stainless Steel, by J. Enoch Johnson and James K. Musick. 20 pp. and figs., May 26, 1967</p> <p>A study was made of the catalytic decomposition of a number of fluorine-containing halogenated hydrocarbons in air, using Hopcalite catalyst in a laboratory-scale reactor which simulates the CO/H₂ burners of nuclear submarines. A few of the highly fluorinated compounds were found to be stable at 305°C. A number of other halogenated hydrocarbons showed substantial decomposition with the production of halogen acids, whereas over stainless steel, a noncatalytic material, very little decomposition occurred. In no case was phosgene observed to be a product. Admixture of</p> <p style="text-align: right;">UNCLASSIFIED (over)</p>	<ol style="list-style-type: none"> 1. Nuclear submarines - Equipment 2. Fluorocarbons - Decomposition 3. Hopcalite - Catalytic properties <p style="text-align: right;">I. Johnson, J. E. II. Musick, J. K.</p>	<ol style="list-style-type: none"> 1. Nuclear submarines - Equipment 2. Fluorocarbons - Decomposition 3. Hopcalite - Catalytic properties <p style="text-align: right;">I. Johnson, J. E. II. Musick, J. K.</p>

UNCLASSIFIED

lithium carbonate with Hopcalite catalyst had no significant effect on the rate of decomposition of the chlorofluorocarbons. Sulfur hexafluoride in air was stable over Hopcalite at temperatures as high as 425 °C.

The results show that use of the chlorofluorocarbons should be as limited as possible in closed environments such as those of nuclear submarines. Where they are needed, as in refrigeration systems, it is recommended that R-114, R-14, or R-12 be used since they show the greatest resistance to Hopcalite-catalyzed decomposition.

UNCLASSIFIED

UNCLASSIFIED

lithium carbonate with Hopcalite catalyst had no significant effect on the rate of decomposition of the chlorofluorocarbons. Sulfur hexafluoride in air was stable over Hopcalite at temperatures as high as 425 °C.

The results show that use of the chlorofluorocarbons should be as limited as possible in closed environments such as those of nuclear submarines. Where they are needed, as in refrigeration systems, it is recommended that R-114, R-14, or R-12 be used since they show the greatest resistance to Hopcalite-catalyzed decomposition.

UNCLASSIFIED

UNCLASSIFIED

lithium carbonate with Hopcalite catalyst had no significant effect on the rate of decomposition of the chlorofluorocarbons. Sulfur hexafluoride in air was stable over Hopcalite at temperatures as high as 425 °C.

The results show that use of the chlorofluorocarbons should be as limited as possible in closed environments such as those of nuclear submarines. Where they are needed, as in refrigeration systems, it is recommended that R-114, R-14, or R-12 be used since they show the greatest resistance to Hopcalite-catalyzed decomposition.

UNCLASSIFIED

UNCLASSIFIED

lithium carbonate with Hopcalite catalyst had no significant effect on the rate of decomposition of the chlorofluorocarbons. Sulfur hexafluoride in air was stable over Hopcalite at temperatures as high as 425 °C.

The results show that use of the chlorofluorocarbons should be as limited as possible in closed environments such as those of nuclear submarines. Where they are needed, as in refrigeration systems, it is recommended that R-114, R-14, or R-12 be used since they show the greatest resistance to Hopcalite-catalyzed decomposition.

UNCLASSIFIED

Security Classification		DOCUMENT CONTROL DATA - R & D	
<i>Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified</i>			
1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
Naval Research Laboratory Washington, D. C., 20390		UNCLASSIFIED	
		2b. GROUP	
3. REPORT TITLE			
STUDIES OF HALOGENATED HYDROCARBONS Part 1 - Stability of Fluorocarbons in Air Over Hopcalite Catalyst or Stainless Steel			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
An interim report on a continuing NRL Problem.			
5. AUTHOR(S) (First name, middle initial, last name)			
J. Enoch Johnson James K. Musick			
6. REPORT DATE		7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
May 26, 1967		20	15
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S)	
NRL Problem C08-30		NRL Report 6546	
b. PROJECT NO.			
SF-013-08-03-4092, 4093, 4094, 4095			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT			
This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Director, Naval Research Laboratory, Washington, D. C. 20390.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
		Department of the Navy (Naval Ships Systems Command) Washington, D. C., 20360	
13. ABSTRACT			
<p>A study was made of the catalytic decomposition of a number of fluorine-containing halogenated hydrocarbons in air, using Hopcalite catalyst in a laboratory-scale reactor which simulates the CO/H₂ burners of nuclear submarines. A few of the highly fluorinated compounds were found to be stable at 305°C. A number of other halogenated hydrocarbons showed substantial decomposition with the production of halogen acids, whereas over stainless steel, a noncatalytic material, very little decomposition occurred. In no case was phosgene observed to be a product. Admixture of lithium carbonate with Hopcalite catalyst had no significant effect on the rate of decomposition of the chlorofluorocarbons. Sulfur hexafluoride in air was stable over Hopcalite at temperatures as high as 425°C.</p> <p>The results show that use of the chlorofluorocarbons should be as limited as possible in closed environments such as those of nuclear submarines. Where they are needed, as in refrigeration systems, it is recommended that R-114, R-14, or R-12 be used since they show the greatest resistance to Hopcalite-catalyzed decomposition.</p>			

