1wp

DR A

Rocketdyne
North American Rockwell

(NASA-CR-129168) TETRAPERCHLORATE OF METHANE Final Report, 11 Mar. 1971 - 10 Mar. 1972 C.J. Schack (Rocketdyne) 30 May 1972 25 p CSCL 07D
N73-11106
Unclas
G3/06 15882

28 pp

Rocketdyne
North American Rockwell

6633 Canoga Avenue,
Canoga Park, California 91304

R-8957

TETRAPERCHLORATE OF METHANE

FINAL REPORT

Contract NAS2-6399

PREPARED BY

C. J. Schack
Exploratory Chemistry

APPROVED BY

E. A. Lawton

E. A. Lawton
Program Manager

NO. OF PAGES 22 & iii

REVISIONS

DATE 30 May 1972

DATE	REV. BY	PAGES AFFECTED	REMARKS

FORM R18-G REV. 5-69

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
ROCKETDYNE
a division of North American Rockwell Corporation
6633 Canoga Avenue, Canoga Park, California 91304

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP
----

3. REPORT TITLE
TETRAPERCHLORATE OF METHANE

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Final Report (11 March 1971 through 10 March 1972)

5. AUTHOR(S) *(First name, middle initial, last name)*
Carl J. Schack

6. REPORT DATE
30 May 1972

7a. TOTAL NO. OF PAGES
25

7b. NO. OF REFS
5

8a. CONTRACT OR GRANT NO.
NAS2-6399

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
R-8957

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
---

10. DISTRIBUTION STATEMENT

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
NASA
Ames Research Center
Moffett Field, California

13. ABSTRACT

The preparation of the tetraperchlorate of methane (TPM) was attempted. Displacement of halogen from carbon tetrahalides was one approach. This was accomplished with either CCl_4 or CBr_4 using the halogen perchlorates, $ClOClO_3$, and $BOClO_3$. Although the displacement process was successful, the generated carbon-perchlorate intermediates were not isolated. Instead, these species decomposed to $COCl_2$, CO_2, and Cl_2O_7. The vigorous displacement reaction that often occurred required moderation. Fluorocarbon solvents and chlorine perchlorate were successfully tested for compatibility, permitting their use in these synthetic reactions. While the sought for moderating effect was obtained, the net result of the displacement of halogen from CX_4 substrates was the same as before. Thus only CO_2, $COCl_2$, and Cl_2O_7 were isolated. These were attributed to the degradation of unstable, intermediate $CX_{4-n}(ClO_4)_n$ species. Tetranitromethane was also examined as a precursor for TPM or mixed nitroperchlorate methanes. However, it was found to be unreactive with Cl_2O_4 in the presence or absence of a solvent.

3.75

DD FORM 1 NOV 65 1473

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
chlorine perchlorates						
oxidizers						
reactions with carbon tetrahalides						

FOREWORD

The research reported herein was supported by the National Aeronautics and Space Administration under Contract NAS2-6399 with Mr. Floyd A. Anderson as the Technical Manager. This report covers the period 11 March 1971 through 10 March 1972. The program has been directed by Dr. D. Pilipovich, Manager, Exploratory Chemistry. Staff members responsible for the scientific effort were Dr. C. J. Schack and Mr. R. D. Wilson. The Program Manager was Dr. E. A. Lawton.

ABSTRACT

The preparation of the tetraperchlorate of methane (TPM) was attempted. Displacement of halogen from carbon tetrahalides was one approach. This was accomplished with either CCl_4 or CBr_4 using the halogen perchlorates, $ClOClO_3$, and $BOClO_3$. Although the displacement process was successful, the generated carbon-perchlorate intermediates were not isolated. Instead, these species decomposed to $COCl_2$, CO_2, and Cl_2O_7. The vigorous displacement reaction that often occurred required moderation. Fluorocarbon solvents and chlorine perchlorate were successfully tested for compatibility, permitting their use in these synthetic reactions. While the sought for moderating effect was obtained, the net result of the displacement of halogen from CX_4 substrates was the same as before. Thus only CO_2, $COCl_2$, and Cl_2O_7 were isolated. These were attributed to the degradation of unstable, intermediate $CX_{4-n}(ClO_4)_n$ species. Tetranitromethane was also examined as a precursor for TPM or mixed nitroperchlorate methanes. However, it was found to be unreactive with Cl_2O_4 in the presence or absence of a solvent.

CONTENTS

INTRODUCTION

The potential enhancement of the energy obtainable from solid propellant ingredients is a subject of continuing interest. Improvements have been sought in several areas including new, more energetic oxidizers. Historically and recently, these efforts have often involved investigations of new perchlorate species, especially perchlorate salts of new and novel bases.

Generally, the attributes of ionic perchlorate materials are well known and documented. However, examples of useful covalent derivatives are fewer and less well defined. In part, the paucity of data for covalent perchlorates is due to the lack of suitable synthetic intermediates able to serve as vehicles for its introduction in substrate molecules. Recently, two new and useful perchlorate compounds were discovered at Rocketdyne (Ref. 1 and 2), which in part fill this void. These compounds are chlorine perchlorate and bromine perchlorate. Both are covalent liquid materials, which are stable below ambient temperature. But most importantly, both compounds are reactive and capable of furnishing perchlorate substituents in covalent or ionic materials.

The objective of this program was the utilization of these perchlorates for the synthesis of the novel, covalent, perchlorate compound, tetraperchloratomethane (TPM). The possible identification and characterization of TPM was aimed at its incorporation in improved propellant systems.

SUMMARY

The synthesis of the tetraperchlorate of methane (TPM) has been attempted under a variety of conditions. In all instances, this objective has been sought using the recently discovered halogen perchlorates, $ClOClO_3$ and $BrOClO_3$, as sources of the perchlorate functionality. The halogen perchlorates were shown to be effective in displacing halogen substituents from the carbon tetrahalides, CBr_4 and CCl_4. This resulted in the formation of free halogen, Cl_2, and Br_2, or mixed halide, BrCl. Generation and measurement of these species was monitored to follow the progress of the reactions. With CCl_4, the displacement reactions proceeded smoothly, but produced unstable intermediates which decomposed to $COCl_2$, CO_2, and Cl_2O_7. With CBr_4, the perchlorate reactions were often uncontrolled, sometimes explosive giving CO_2 and Cl_2O_7. Controlled reactions in these systems was sought using selected fluorocarbons as solvents. Chlorine perchlorate was shown experimentally to be soluble in and compatible with the chosen solvents. Carbon tetrachloride and Cl_2O_4 in solution still produced only the degradation products CO_2, $COCl_2$, and Cl_2O_7. Their rate of formation varied with different solvents but intermediate $C\text{-}OClO_3$ species were not detected. Carbon tetrabromide and Cl_2O_4 in solution reacted rapidly but in a nonexplosive manner. From these reactions, however, only CO_2, Cl_2O_7 and elemental halogen were consistently isolated. Thus, the solvents did not stabilize intermediate perchloratomethanes. The stoichiometry and products of these displacement reactions are most readily interpreted in terms of the formation and decomposition of the intermediates $CX_{4-n}(ClO_4)_n$, where n=2,4.

An alternate substrate, $C(NO_2)_4$, was also reacted with Cl_2O_4 to form TPM. In this case, no displacement reaction was observed under any of the conditions tried including solution reactions.

DISCUSSION

Chlorine perchlorate, $ClOClO_3$ (or empirically Cl_2O_4), is a reactive molecule and an excellent source of the perchlorate group in anhydrous environments. Elementary examples of this reactivity are shown by the equations:

$$HCl(\text{anhydrous}) + Cl_2O_4 \longrightarrow HClO_4 + Cl_2$$

$$CsCl + Cl_2O_4 \longrightarrow CsClO_4 + Cl_2$$

$$AgCl + Cl_2O_4 \longrightarrow AgClO_4 + Cl_2$$

All of these reactions are related in that the positively polarized terminal chlorine from Cl_2O_4 combines with a negative chlorine to drive the reaction to completion. Furthermore, both covalent and ionic "chloride" species react and perchlorates are formed. Bromine perchlorate, $BrOClO_3$ or emprically $BrClO_4$, also reacts in this manner to provide perchlorates accompanied by the evolution of BrCl.

Extension of the above method was carried out with methylchloride and chlorine perchlorate.

$$CH_3Cl + Cl_2O_4 \longrightarrow CH_3OClO_3 + Cl_2$$

Methylperchlorate was readily formed at temperatures below ambient. Methylene chloride behaved similarly, liberating Cl_2 and forming mono- and bis-perchlorate derivatives.

Overall, this type of reactivity for the halogen perchlorates appeared quite akin to that of the analogous compounds, chlorine fluorosulfate and bromine fluorosulfate. For example, it was reported (Ref. 3) that bromine fluorosulfate could condense with chlorocarbons to form polyfluorosulfatomethanes:

$$CCl_4 + 4BrOSO_2F \longrightarrow C(OSO_2F)_4 + 4BrCl$$

Quite interestingly, it was noted during this work that the order of increasing stability for the series of fluorosulfatomethanes, $CCl_{4-x}(SO_3F)_x$, was $X = 1 < X = 2 < X = 3 < X = 4$. Thus the tetrakis compound was the most stable. With this knowledge, a similar route to the potentially very dense and energetic tetraperchloratomethane was clearly indicated.

$$CCl_4 + 4XOClO_3 \longrightarrow C(OClO_3)_4 + 4XCl \text{ (X = Br, Cl)}$$

In addition to carbon tetrachloride it seemed likely that carbon tetrabromide could also serve as a starting material

$$CBr_4 + 4XOClO_3 \longrightarrow C(OClO_3)_4 + 4BrX \text{ (X = Br, Cl)}$$

The formation of Br_2 in this type reaction had not been experimentally verified, but it was reported for covalent bromide-$BrSO_3F$ reactions (Ref. 3). Thus, in these reactions the difference in polarity of the halogen attached to carbon and that bonded to the perchlorate whether it be chlorine or bromine is utilized to promote the reaction.

A final compound considered and used for the possible synthesis of TPM was tetranitromethane. In place of the foregoing schemes involving substitution of carbon-halogen bonds, tetranitromethane offered the weaker C-N bond for substitution.

$$C(NO_2)_4 + 4ClOClO_3 \longrightarrow C(OClO_3)_4 + 4ClNO_2$$

The coproduct $ClNO_2$ does not provide an appreciably enhanced driving force for this reaction. However, it was an attractive alternate because substitution of the weaker C-N link might require a lower activation energy. Also, even partially substituted intermediates, i.e., mixed nitroperchloratomethanes might be useful materials in propellant applications.

ACQUISITION OF STARTING MATERIALS

The halogen perchlorates are not commercial materials and must be prepared. Also, some of the reagents required for the synthesis of Cl_2O_4, namely ClF and $ClSO_3F$ were prepared. The overall preparative scheme is shown in the equations:

$$Cl_2 + ClF_3 \xrightarrow{\Delta} 3ClF$$

$$ClF + SO_3 \longrightarrow ClSO_3F$$

$$ClSO_3F + Cs^+ClO_4^- \longrightarrow ClOClO_3 + Cs^+SO_3F^-$$

Chlorine monofluoride is stable at ambient temperature and was made in sufficient amount, in one run, for the duration of the program. Purified ClF was reacted with SO_3 to form $ClSO_3F$, which is also storable at ambient conditions. Finally, purified $ClSO_3F$ was used to obtain Cl_2O_4 by contacting liquid $ClSO_3F$ with excess $CsClO_4$ at approximately -45 C for several days. The conversion is approximately quantitative although 2 to 3 percent of unreacted $ClSO_3F$ has sometimes been encountered.

Chlorine perchlorate is not stable for long periods at ambient temperature and is shock sensitive. However, it can be stored indefinitely at approximately -30 C or lower. Therefore, because low temperature storage space is limited and because safety considerations prohibit keeping too large a quantity of Cl_2O_4 in one place, this compound was made in multiple, small (9 mmole) batches on a periodic basis.

Bromine perchlorate can be prepared from $BrSO_3F$ and $CsClO_4$ but it is difficult to transfer without partial decomposition. Therefore it is better to synthesize it according to the reaction:

$$Br_2 + 2ClOClO_3 \longrightarrow 2BrOClO_3 + Cl_2$$

Removal of by-product Cl_2 affords pure $BrClO_4$ in a container to which a reactant may be added and thus eliminating the necessity for $BrClO_4$ transfers.

Carbon tetrachloride used for the program was the best quality spectrograde material and was shown to be pure by gas chromatography and infrared analysis. Carbon tetrabromide was also purchased and was purified by vacuum sublimation. Tetranitromethane was acquired in-house and was of good purity as shown by infrared and chromatographic analysis.

GENERAL METHOD OF REACTION

Clean, dry, prepassivated (with ClF_3) stainless-steel cylinders or FEP Teflon ampoules equipped with a stainless-steel valve were used as reactors. Substrates were measured either volumetrically in a calibrated vacuum line (e.g., CCl_4) and condensed into the reactor or gravimetrically in a dry box and frozen in the reactor. Excess Cl_2O_4 over the 4:1 ratio needed for complete reaction was loaded from the vacuum line into the reactor at -196 C. For $BrClO_4$ reactions, the order of addition was reversed since the $BrClO_4$ was formed _in situ_ first. The selected reaction temperature was approached by initially warming to -80 C for 2 to 3 hours before completing the warmup to the final temperature.

To follow the course of the reactions expeditiously and to minimize handling of the halogen perchlorates, the following experimental procedure was usually employed. After a predetermined reaction period, the reactor was attached to a vacuum line and cooled to liquid nitrogen temperature (-196 C). The reactor was then opened to the gage and the presence (or absence) of noncondensible gases; i.e., O_2, noted. This was pumped away and the reactor warmed to -80 C, while continuing to pump through a series of U-traps cooled to -112 and -196 C, thereby separating volatile by-products. Because Cl_2 and BrCl, the most common by-products, are more volatile than the starting materials or TPM, the amount of them produced was monitored to assay the extent of the substitution reaction.

CARBON TETRACHLORIDE-CHLORINE PERCHLORATE REACTIONS

The initial reactions of carbon tetrachloride and chlorine perchlorate were conducted in stainless-steel cylinders, in the absence of a solvent at approximately -45 or -25 C. Because of the low reaction temperatures and because four substitutions were necessary, it was expected that a slow reaction would occur. Therefore, monitoring of the quantity of evolved Cl_2 was performed at 1 week or longer intervals. For the -45 C reaction, several such measurements were carried out over a 7-week period. Each time little or no -196 C noncondensible gas was found and a continuous, slow generation of Cl_2 was evident. However, the evolved Cl_2 was accompanied by phosgene, $COCl_2$, which presumably arose from the undesired reaction:

$$CCl_4 + 2Cl_2O_4 \longrightarrow Cl_2C(OClO_3)_2 + 2Cl_2$$

$$Cl_2C(OClO_3)_2 \longrightarrow COCl_2 + Cl_2O_7$$

Based on the observed Cl_2 and $COCl_2$, it was apparent that nearly all the remaining CCl_4 should have been reacted to give TPM.

This encouraging observation was countered by the fact that more Cl_2O_7 was present than could be accounted for by phosgene forming reaction sequence. Further workup revealed the presence of still more Cl_2O_7, together with unreacted Cl_2O_4 and some CO_2. No carbon-perchlorate material was found and no nonvolatile product was observed. The poor material balance for the reaction with respect to carbon species was attributed to the loss of small increments of CO_2 during the Cl_2 monitoring experiments. The Cl_2 fractions were examined by infrared spectroscopy which had not revealed any CO_2. However, the infrared absorbance of CO_2 is relatively low and this apparently allowed it to pass undetected. As the individual separations of Cl_2 were discarded, there was no cumulative concentration of CO_2, which would have permited its detection.

On repeating the CCl_4-Cl_2O_4 reaction at -45 C, all volatile, condensible material removed from the reactor, after checking for Cl_2 generation, was returned. In this fashion, it was determined that CO_2 was formed in an appreciable amount during the course of the reaction. Thus, in this second experiment, after approximately 4 weeks, all the CCl_4 was reacted, giving CO_2 and $COCl_2$ in yields of 30 and 70 percent, respectively. The remaining products were Cl_2, Cl_2O_7, and unreacted Cl_2O_4. Oxygen, which would be indicative perhaps of an uncontrolled reaction, was not a product.

The interaction of CCl_4 and Cl_2O_4, which was carried out at approximately -25 C, was not appreciably different in its outcome than those at -45 C. Here, again, after 7 weeks, a thorough vacuum fractionation of the volatile materials showed that all the charged CCl_4 had been reacted. However, CO_2 was the predominant carbon-containing product (96.5 percent) with the remainder being $COCl_2$. Also formed in high yield were Cl_2 and Cl_2O_7. Only trace quantities of the by-products ClO_2 and $FClO_3$ were found. The very good material balance obtained for these components indicated no nonvolatile species such as TPM could have remained in the cylinder; a fact confirmed gravimetrically and visually in the dry box.

Considering the products observed in these reactions of CCl_4 and Cl_2O_4, it is certainly obvious that a displacement reaction involving elimination of Cl_2 and substituion of ClO_4 did occur. However, this desired reaction was apparently succeeded by other occurrences as outlined in the sequences below:

a.
$$CCl_4 + 4Cl_2O_4 \longrightarrow 4Cl_2 + [C(OClO_3)_4]$$
$$[C(OClO_3)_4] \longrightarrow CO_2 + 2Cl_2O_7$$

b.
$$CCl_4 + 2Cl_2O_4 \longrightarrow 2Cl_2 + [Cl_2C(OClO_3)_2]$$
$$[Cl_2C(OClO_3)_2] \longrightarrow COCl_2 + Cl_2O_7$$
$$COCl_2 + 2Cl_2O_4 \longrightarrow 2Cl_2 + [OC(OClO_3)_2]$$
$$[OC(OClO_3)_2] \longrightarrow CO_2 + Cl_2O_7$$

Both of these paths imply an instability for certain perchlorated derivatives, which is, of course, undesired.

Other, more-complicated reaction schemes are also possible that could account for the observed products. For example, the formation of $COCl_2$ could result from the sequence:

c.
$$CCl_4 + Cl_2O_4 \longrightarrow Cl_2 + Cl_3COClO_3$$
$$Cl_3COClO_3 + Cl_2O_4 \longrightarrow Cl_2O_7 + [Cl_3COCl]$$
$$[Cl_3COCl] \longrightarrow Cl_2 + COCl_2$$

In this case only mono-substitution of the CCl_4 occurs, followed by reaction with additional Cl_2O_4 to generate Cl_2O_7 and the unstable hypochlorite. The hypochlorite would then spontaneously eliminate Cl_2 to produce $COCl_2$. However, no example of a $C\text{-}OClO_3$ behaving in this fashion has been demonstrated, e.g., R_fOClO_3 species are stable in the presence of Cl_2O_4 (Ref. 4). Also C-OCl moieties have never been obtained in this manner. Thus, this reaction path seems less likely than the preceding cases as a route to $COCl_2$ and/or CO_2.

Whether this apparent instability of perchlorated methanes is inherent or whether it was perhaps catalyzed, e.g., by a metal fluoride surface layer is the reaction cylinder, was examined. To test this thesis, CCl_4 and Cl_2O_4 were reacted in a Pyrex container at approximately -55 C for 8 weeks. Assaying the reaction at that time revealed about 35 percent of the theoretical amount of Cl_2 had been formed. Phosgene was also present in about 15 percent yields. Carbon dioxide was produced but leakage of Teflon fittings on the glass reactor prevented a meaningful measurement since CO_2 leaked in from the dry-ice coolant. Nevertheless this experiment demonstrated that the metal container did not inhibit the reaction or promote decomposition of any formed $C\text{-}OClO_3$ materials, since the results for the Pyrex container were not materially different.

To determine whether the reaction rate of $COCl_2$ and Cl_2O_4 is such that it might account for the formation of CO_2 in these systems, the interaction of those materials was investigated. At -45 C it was observed that a 1- to 2-week reaction produced significant amount of CO_2, accompanied by Cl_2 and Cl_2O_7 and loss of $COCl_2$.

No carbon-perchlorate compounds or other unknown materials were noted. Thus, under these conditions, phosgene and chlorine perchlorate react moderately and directly to furnish CO_2.

CARBON TETRABROMIDE-CHLORINE PERCHLORATE REACTIONS

As pointed out earlier, the formation of BrCl in the CCl_4-$BrSO_3F$ reaction was useful in producing $C(SO_3F)_4$ (Ref. 3). Therefore, the formation of BrCl from the CBr_4-Cl_2O_4 system was expected to be useful in producing TPM. The initial investigations of this reaction were in the stainless-steel reactors at three different temperatures, -45, -55, and -80 C. The amount of Cl_2O_4 was well in excess of that required for replacement of all the C-Br bonds. Monitoring for BrCl was not as precise as for Cl_2 because of competing side reactions. The reactions that were expected to occur are:

$$CBr_4 + 4Cl_2O_4 \longrightarrow C(ClO_4)_4 + 4BrCl$$

$$2BrCl \rightleftharpoons Br_2 + Cl_2$$

$$Br_2/BrCl + Cl_2O_4 \longrightarrow BrClO_4 + BrCl/Cl_2$$

On examination, it was found that the course of the reaction varied, sometimes being uncontrolled. The -45 C experiment after 16 days gave no O_2, but all the CBr_4 used was recovered as CO_2. Other products were Cl_2O_7, $X_2(Cl_2, Br_2, BrCl)$, and $BrClO_4$. The vigorous character of this reaction, hinted at by the complete conversion to CO_2, was confirmed by the -55 C experiment. In this instance, for the first time, oxygen was produced and in very large amount, together with an approximately quantitative yield of CO_2. To moderate the reaction, it was repeated again but at -80 C, i.e., in direct contact with solid CO_2 for the entire reaction period of 1 month. This time, no O_2 was formed but again CO_2 was obtained equivalent to all the CBr_4 used. The oxides, Cl_2O_7 and $BrClO_4$, were also produced as expected, as well as bromine, chlorine, and BrCl.

These results did indicate that bromine was quite susceptible to displacement by ClO_4. What was required was to provide the proper environment for stabilizing the resultant mixed Br-C-ClO_4 moieties so that all the bromines could be substituted.

Here again, the metal container was suspect as a possible catalytic surface influencing decomposition of the intermediates. Accordingly, an experiment was set up in a Teflon container. Solid CBr_4 was placed at the bottom of the Teflon tube and Cl_2O_4 condensed at -196 C in a ring higher up the tube. On transferring the closed reactor from -196 C to a dry ice chest (-80 C), an explosion occurred. In the brief time period involved, it is estimated that the reactor could not have risen much above the melting point of Cl_2O_4 ($\sim$-115 C).

Repetition of the reaction on the same scale was carried out with further moderation of the rate of temperature rise to preclude this runaway interaction. To accomplish this, the loaded reactor, while still at -196 C, was placed in a liquid nitrogen-dry ice slush. (After the LN_2 evaporates, a relatively large mass of CO_2 solid remains frozen at -196 C around the tube. In a dewar, this mass slowly heats up to the sublimation point of CO_2 which is then easily maintained.) In this way, a slow, efficient warming of small chemical reactions is readily obtained.

The CBr_4-Cl_2O_4 system, however, still proved unresponsive to this slow warmup. Approximately 20 hours after placing the tube in the LN_2/CO_2 bath, when the temperature was presumed to be approaching -80 C, the reactants again exploded. It appears then that the thermal insulative properties of Teflon were too great to permit adequate removal of the heat generated. To overcome this above problem, a solvent was employed for the reaction. The solvent not only provides a diluent effect, but through mass and heat transfer effects, assists in dissipating the heat of the reaction.

CARBON TETRACHLORIDE-BROMINE PERCHLORATE REACTIONS

Attempted syntheses of TPM involving $BrClO_4$ as an intermediate were not studied as extensively as the Cl_2O_4 system. This is due to the fact that $BrClO_4$ can only be prepared from Cl_2O_4 and obviously use of the latter eliminates then one step in the overall preparation of TPM. Nevertheless, some experiments have employed $BrClO_4$ to uncover any possible, but unknown, advantages it might offer. These experiments used CCl_4 as a substrate and thus the formation of BrCl was expected, together with the side reactions cited above which are peculiar to BrCl itself and in this environment.

The initial experiment was conducted at about -20 C for 11 days. At that time, it was found that complete reaction of the CCl_4 had occurred. However, the observed carbon-containing products ($COCl_2$, 59%; CO_2, 22%; COFCl, 19%) again indicated a somewhat vigorous reaction had occurred. In addition to these materials, Br_2, Cl_2, and Cl_2O_7 were the main products, along with a minor amount of $FClO_3$. The fluorine containing compounds noted are probably formed through reactions with a metal fluoride passivation layer present in the cylinder. The deleterious effect of this on the course of the reaction is unknown, but the amount of COFCl formed points to an appreciable interference.

Another reaction of CCl_4 with $BrClO_4$ was carefully maintained at -80 C to slow the substitution process and help stabilize intermediate species. Here no noteworthy amounts of fluorinated compounds were formed and more extensive substitution of C-Br bonds occurred. However, nearly all the available carbon was converted to CO_2 (~93 percent). The usual by-products, Br_2, Cl_2, BrCl, Cl_2O_7, and $BrClO_4$ were also found. No solid or liquid product remained in the reactor. Thus, it appears again that reactions involving the generation of BrCl occur readily and completely, but that they are too exothermic or the intermediates too unstable to allow isolation of the desired TPM. Further reactions of mixtures involving $BrClO_4$ and furnishing BrCl were not conducted. Systems involving generation of BrCl as a by-product were limited to CBr_4-Cl_2O_4.

TETRANITROMETHANE-CHLORINE PERCHLORATE REACTIONS

While the carbon tetrahalide compounds received the primary attention as precursors to TPM, the alternate substrate, tetranitromethane (TNM) was also examined. With chlorine perchlorate, the reaction sought was:

$$C(NO_2)_4 + 4Cl_2O_4 \longrightarrow C(ClO_4)_4 + 4ClNO_2$$

Nitrylchloride is comparable in volatility to Cl_2 and thus could be monitored in the same way that Cl_2 was to follow the course of the reaction. However, nitrylchloride is susceptible to decompostion, especially in metal, as shown by the equation:

$$2ClNO_2 \longrightarrow Cl_2 + N_2O_4$$

Thus, Cl_2 or $Cl_2/ClNO_2$ mixtures were considered as likely observable products with the monitoring technique employed. In all, after 2 weeks at -45 C and 4 weeks at -25 C, the only volatile by-product noted was Cl_2 (11 to 12 percent of theory). Further workup did not reveal any $ClNO_2$, N_2O_4 or other species to indicate replacement of an NO_2 group from TNM. Chlorine perchlorate and TNM were recovered along with a small amount of Cl_2O_7. No product less volatile than TNM was observed.

Overall, it appeared certain that no reaction occurred other than a limited amount of decomposition of the Cl_2O_4. The fact that TNM is a solid at the reaction temperature and was probably not dissolved by the Cl_2O_4 undoubtedly hindered the reaction. Better mixing and contact of the reactants required a mutual solvent.

SOLVENTS

The initial reactions aimed at preparing TPM amply demonstrated that a solvent was necessary to achieve maximum utility for the potential reactants. On the one hand, the CBr_4 reactions were uncontrollable and even explosive in the absence of a solvent. And on the other hand TNM was unreactive possibly due to poor contact with Cl_2O_4 while solid at the appropriate reaction temperature.

Since the halogen perchlorates are reactive toward C-Cl and C-Br bonds and since C-H links might act as fuels for these oxidizers, the list of potential solvents was limited in general to perfluorinated materials. Furthermore, possible solvents for the halogen perchlorates must not contain any olefin links and also probably not any unsaturation as in a cyanide group. This is due to the fact that the $XClO_4$ compounds can add readily to such unsaturated links (Ref. 4).

Three fluorocarbon liquids were selected for testing as potential solvents for Cl_2O_4. These were FC-43, FC-78, and Freon E-2. The first is perfluorotributyl amine, a relatively nonvolatile (b.p., 178 C) liquid permitting easy separation of volatile by-products. The second is a mixture of C_6F_{14} and cyclo $C_6F_{12}O$ which is moderately volatile (b.p., ~50 C), but which is still liquid at about -80 C. The E-2 liquid is $CF_3CF_2CF_2OCF(CF_3)CF_2OCHFCF_3$, which is of intermediate volatility (b.p., 104 C), but which has a pour point of -123 C, giving it a very long and useful low temperature liquidus range. While the E-2 compound does have one C-H link, this should be shielded and inert enough not to react with the perchlorates. Gas chromatography of the liquids showed no impurities in the FC-75, about 0.25 percent total impurity in the E-2, and less than 1 percent total impurity in the FC-43. They were used without further purification.

Compatibility tests were started with approximately 1 milliliter of these liquids in a Teflon tube equipped with a stainless-steel valve. Chlorine perchlorate (~1.3 mmole) was added to each and the tubes were then kept at -45 or -25 C. All three solvents gave a homogeneous, yellow-colored solution of the Cl_2O_4. All three solvents were found not to have reacted with the Cl_2O_4 after a minimum of 4 weeks at each temperature. This was verified by the failure of each to generate O_2, Cl_2, or any other chlorine oxide at the end of that period. (Only when volatiles were removed from the compatibility test ampoules and then recondensed in after analysis was decomposition of Cl_2O_4 sometimes observed. This was ascribed to impurity addition or formation due to incomplete passivation.)

Having established the compatibility of Cl_2O_4 and the selected solvents, it was necessary to determine the approximate solubilities of the CX_4 materials in them. These tests were not quantitative but were of sufficient accuracy to avoid certain or significant precipitation. The results are summarized in the following tabulation.

Approximate Solubility Limits

	CCl_4 mmole/ml at -15 C	CBr_4 mmole/ml at 0 C	$C(NO_2)_4$ mmole/ml at -25 C
FC-78	1.0	0.015	1.0
E-2	1.0	0.012	0.7
FC-43	0.35	0.007	0.5

Carbon tetrabromide is much the least soluble compound and FC-43 is the poorest solvent.

REACTIONS IN SOLVENTS

All of the attempts to synthesize TPM, which used a solvent, were conducted in FEP Teflon ampoules. In this way it was possible to note the presence or absence or more than one phase, discolorations, etc. Carbon tetrachloride-chlorine perchlorate reactions were carried out in all three solvents. In general, there does not appear to have been any dramatic affect of the solvents on this reaction compared to those examples wherein no solvent was used. Thus with FC-43: at -45 C, $COCl_2$ was the principal carbon containing products with a lesser amount of CO_2 being observed; at -25 C, CO_2 was nearly the exclusive product. Chlorine and Cl_2O_7 were the only other significant species. These results are again in keeping with the reactions.

$$CCl_4 + 2Cl_2O_4 \longrightarrow COCl_2 + 2Cl_2 + Cl_2O_7$$

$$CCl_4 + 4Cl_2O_4 \longrightarrow CO_2 + 4Cl_2 + 2Cl_2O_7$$

Carbon tetrachloride was not completely reacted in 4 weeks at -45 C when insufficient solvent was present to completely dissolve it.

With Freon E-2 as a solvent these reactants were even less reactive. At -45 C in this case, approximately 45 percent of the CCl_4 only reacted in 4 weeks to give $COCl_2$ and CO_2. Even at -25 C for the same period about 8 percent of the

CCl_4 was recovered together with 42 percent $COCl_2$ and 50 percent CO_2. Chlorine was found commensurate with the foregoing observed quantities of $COCl_2$ and CO_2. Chlorine heptoxide however, was not fully separable from the solvent and therefore was not measured.

Finally, CCl_4 and Cl_2O_4 idssolved in FC-78 reacted quite completely after 4 weeks at both -45 and -25 C. This was evidenced by essentially quantitative conversion to CO_2 at either temperature. Chlorine was measured to confirm the usual stoichiometry of this system but Cl_2O_7, although identified, could not be separated from the solvent and measured.

The foregoing results for these components make evident the fact that their preferred reaction path leads ultimately to the formation of CO_2, Cl_2, and Cl_2O_7. In each case examined, with or without solvent, carbon tetrachloride and chlorine perchlorate have yielded only CO_2 or COX_2 as carbonaceous products. Further effort to use this system to synthesize TPM is not warranted.

Carbon tetrabromide and ClO_4 were reacted using E-2 and FC-78 as solvents. These liquids did have a moderating effect on the reaction as shown by the fact that explosions were not encountered under conditions where they had occurred previously. These reactions were run at -25 C for 1 to 2 weeks. The reaction may have been complete sooner since no visible change occurred after the first day or so. At that time the reaction mixture contained two liquid phases. The lower one was of less volume and very dark red. The upper was orange and was mainly solvent. Partial separation of the products showed CO_2 equivalent to the starting material, CBr_4, together with twice as much Cl_2. These materials would arise from the reaction.

$$CBr_4 + 4Cl_2O_4 \longrightarrow CO_2 + 2Cl_2 + 2Br_2 + 2Cl_2O_7$$

The lower, dark red phase was mainly Br_2 and Cl_2O_7 together with some $BrClO_4$ formed from the reaction of excess Cl_2O_4 and Br_2. Therefore here also as with CCl_4, no stable carbon-perchlorate was obtained. Substitution for C-Br took place but gave only degradation products as isolable species.

With TNM and Cl_2O_4 in each of the three solvents homogeneous solutions were prepared. Nevertheless, even after several weeks at -25 C no evidence for displacement of NO_2 was found. Either nothing ensued or a limited amount of decomposition of Cl_2O_4 occurred. Therefore, even in intimate contact in solution, TNM does not react with Cl_2O_4.

CONCLUSION

Despite all efforts to prepare tetraperchloratomethane by simple substitution reactions using CX_4 substrates and halogen perchlorates, neither TPM nor any other $CX_{4-n}(ClO_4)_n$ moiety was isolated. Instead, in all cases where reaction took place, the CX_4 molecule was converted to CO_2 or to mixtures of CO_2 and COX_2. These degradation products were accompanied by the formation of Cl_2O_7. From these uniform results it appears that TPM and its related perchlorated methanes are both kinetically and thermodynamically unstable and incapable of independent existence under these conditions of formation.

EXPERIMENTAL

APPARATUS

Volatile materials were separated or purified using a calibrated stainless-steel vacuum line equipped with FEP-Teflon U-trap and Heise Bourdon tube-type pressure gage. Infrared spectra of gases were obtained using 5-cm path length stainless-steel cells fitted with AgCl windows. Spectra were recorded over the range 4000 to 250 cm^{-1} on a Perkin-Elmer Model 337 Infracord. Gaseous compounds were separated and analyzed on a Rocketdyne-built gas chromatograph operating at ambient temperature with 25 psi helium at 25 cc/min and with 3/16-inch x 16.4-foot column filled with 25 percent perfluorokenosene or Fluoropak 80. Retention times (in minutes) for some compounds of interest: CO_2, 2.8; Cl_2, 3.9; $FClO_3$, 5.5; $COCl_2$, 8.7. Liquids were analyzed on a Hewlett-Packard Model 700 chromatograph equipped with temperature programming and automatic attenuation. A 3/16-inch x 11-foot column packed with 3 percent QF-1 on Chromasorb-T.

SYNTHETIC REACTIONS

The following reactions are typical and representative examples of the syntheses conducted during the program.

PREPARATION OF CHLORINE MONOFLUORIDE

A 1 liter stainless-steel cylinder was loaded at -196 C with approximately 12.5 liters each of gaseous Cl_2 and ClF_3 (from the Matheson Co.). After warming to ambient temperature, the reactor was electrically heated overnight at about 150 C. After recooling to room temperature, the product ClF was stored until needed. Purification as it was used was accomplished by fractionation through U-traps cooled to -142 and -196 C. The material retained at -196 C was then reacted with SO_3.

PREPARATION OF CHLORINE FLUOROSULFATE

Purified ClF was condensed onto SO_3 (Allied Chemical Co.) contained in a 150-milliliter stainless-steel cylinder (Ref. 5). Generally, a 0.2 mole scale was used with about a 10-percent excess of ClF. The reaction was completed by slow warming of the reactor to ambient temperature. Purification of $ClSO_3F$ was affected by vacuum fractionation through U-traps cooled to -80, -112, and -196 C. The middle fraction was employed in the formation of chlorine perchlorate.

PREPARATION OF CHLORINE PERCHLORATE

A 30-milliliter stainless-steel cylinder that had been passivated with ClF_3 was loaded in the dry box with 4.0 g ($\sim$16 mmole) of anhydrous $CsClO_4$ (Research Inorganic Chemical Corp.). The evacuated cylinder was then charged with purified $ClSO_3F$ ($\sim$10 mmole) at -196 C. Warming to -45 C for 2 days or until needed furnished chlorine perchlorate. This compound was purified immediately prior to use by fractionation through U-traps kept at -80, -112, and -196 C. Chlorine perchlorate was retained at -112 C. The yield was usually 90 to 95 percent ($\sim$9 mmole).

PREPARATION OF BROMINE PERCHLORATE

Bromine (1.82 mmole) was loaded into a prepassivated 30-milliliter stainless-steel cylinder at -196 C followed by Cl_2O_4 (3.69 mmole). After several days at -45 C, the by-product Cl_2 and excess Cl_2O_4 were removed by first pumping on the cylinder at -80 C for 1 hour then at -64 C for 10 minutes. The total amount of Cl_2 produced (1.74 mmole) indicated a nearly quantitative conversion to $BrClO_4$ which was retained in the cylinder.

CCl_4-Cl_2O_4 WITHOUT SOLVENT

A 30-milliliter stainless-steel cylinder was loaded with CCl_4 (2.00 mmole) followed by freshly purified Cl_2O_4 (9.55 mmole), both at -196 C. After warming first to -80 C for a short time, the reactor was kept at approximately -25 C for

32 days. Upon recooling to -196 C, some noncondensible O_2 was found (~ 0.4 mmole). While warming to ambient temperature, the contents of the reactor were separated by fractional condensations under vacuum in a series of U-traps cooled to -45, -80, -112, and -196 C. The various fractions were measured and identified by their infrared spectra and G.C. elution times. The products were (in mmoles): CO_2, 1.93; $COCl_2$, 0.07; Cl_2, 8.65; Cl_2O_7, 3.34; Cl_2O_4, 0.98; and $ClO_2/FClO_3$, 0.55. No residue remained in the reactor. The yields were 96.5 percent CO_2 and 3.5 percent $COCl_2$ accounting for all the CCl_4 used.

CBr_4-Cl_2O_4 WITHOUT SOLVENT

Using the same procedure as above, CBr_4 (1.54 mmole) and Cl_2O_4 (8.27 mmole) were reacted at -80 C for 33 days. Multiple fractional condensations in traps cooled to -80, -112, and -196 C was followed by measurement and identification of the products. These were (in mmole): CO_2, 1.54; X_2 (Cl_2, BrCl, Br_2), 7.51; Cl_2O_7, 1.41; and a mixture of $Cl_2O_7/ClO_2/BrClO_4$, ~2.44. All the CBr_4 was converted to CO_2 and no C-ClO_4 products were observed.

CCl_4-$BrClO_4$ WITHOUT SOLVENT

Bromine perchlorate (~3.66 mmole) was prepared and purified in a 30-milliliter cylinder. Carbon tetrachloride (0.79 mmole) was added at -196 C from the vacuum line and the reaction then maintained at -80 for 32 days. At no time was O_2 found to have been formed. Volatile products were separated by fractionation as before while warming the cylinder to 0 C. The observed products were CO_2 (0.74 mmole) and traces of $COCl_2$ together with much Cl_2, BrCl, Br_2, and Cl_2O_7. The high yield of CO_2 (93 percent) accounted for nearly all the starting CCl_4. Inspection of the cylinder in the dry box showed no nonvolatile liquids or solids were left and no evidence for TPM was obtained.

CCl_4-Cl_2O_4 IN FC-43

Into a Teflon ampoule containing CCl_4 (0.98 mmole) and about 3 milliliters of FC-43 was loaded Cl_2O_4 (4.87 mmole). The reaction was allowed to proceed at -25 C for 4 weeks. Only a minor trace of O_2 was found in the reactor at the end of that period. As before, fractional condensations showed the products volatile at 0 C (the temperature to which the reactor was finally raised) were (in mmole): CO_2, 0.95; $COCl_2$/COFCl, trace; Cl_2, 3.97; together with a little unreacted Cl_2O_4 and by-product Cl_2O_7, which was mixed with some FC-43 which had distilled from the reactor. Again the nearly quantitative yield of CO_2 indicated no TPM was present. An infrared spectrum of the liquid reactor residue showed only FC-43.

CBr_4-Cl_2O_4 IN FREON E-2

A reaction of CBr_4 (1.04 mmole) and Cl_2O_4 (4.41 mmole) was carried out in a Teflon ampoule using 3 milliliters of Freon E-2. After 1 week at -25 C, the reaction was worked up by appropriate fractionations. The less volatile products, e.g., Cl_2O_7, Br_2, $BrClO_4$, were not fully separable from the solvent but their presence was indicated visually and by infrared analyses. The more-volatile species were cleanly separated. These were CO_2 (1.04 mmole) and Cl_2 (1.82 mmole). All the CBr_4 was converted to CO_2.

$C(NO_2)_4$-Cl_2O_4 IN FREON E-2

Tetranitromethane (1.15 mmole) and Cl_2O_4 (5.56 mmole) were reacted in a Teflon ampoule at -25 C for 3 weeks using 3 milliliters of Freon E-2 as the solvent. Recooling to -196 C at the end of this period showed about 0.1 mmole of O_2 formed. Fractionation on warming to 0 C allowed Cl_2 to be separated (0.44 mmole). Unreacted Cl_2O_4 constituted the only other isolated material. Therefore, apart from a very little Cl_2O_4 decomposition, no other reaction was observed.

REFERENCES

1. C. J. Schack and D. Pilipovich, Inorg. Chem., 9, 1387 (1970).
2. C. J. Schack, K. O. Christe, D. Pilipovich, and R. D. Wilson, ibid., 10, 1078 (1971).
3. D. D. des Marteau, ibid., 7, 434 (1968).
4. R-8234, Final Report, Inorganic Halogen Oxidizers, Contract Nonr 4428(00), 31 May 1970, CONFIDENTIAL.
5. C. J. Schack and R. D. Wilson, Inorg. Chem., 9, 311 (1970).