UNCLASSIFIED/~~LIMITED~~

Policy on the Redistribution of DTIC-Supplied Information

~~As a condition for obtaining DTIC services, all information received from DTIC that is not clearly marked for public release will be used only to bid or perform work under a U.S. Government contract or grant or for purposes specifically authorized by the U.S. Government agency that is sponsoring access. Further, the information will not be published for profit or in any manner offered for sale.~~

~~Non-compliance may result in termination of access and a requirement to return all information obtained from DTIC.~~

NOTICE

We are pleased to supply this document in response to your request.

The acquisition of technical reports, notes, memorandums, etc., is an active, ongoing program at the **Defense Technical Information Center (DTIC)** that depends, in part, on the efforts and interest of users and contributors.

Therefore, if you know of the existence of any significant reports, etc., that are not in the **DTIC** collection, we would appreciate receiving copies or information related to their sources and availability.

The appropriate regulations are Department of Defense Directive 3200.12, DoD Scientific and Technical Information Program; Department of Defense Directive 5230.24, Distribution Statements on Technical Documents; American National Standard Institute (ANSI) Standard Z39.18-1987, Scientific and Technical Reports- Organization,Preparation,and Production;Department of Defense 5200.1-R, Information Security Program Regulation.

Our **Programs Management Branch, DTIC-OCP**, will assist in resolving any questions you may have concerning documents to be submitted. Telephone numbers for that office are **(703) 274-6847**, or **DSN 284-6847**. The **Reference Services Branch, DTIC-BCR**, will assist in document identification, ordering and related questions. Telephone numbers for that office are **(703) 274-7633** or **DSN 284-7633**.

DO NOT RETURN THIS DOCUMENT TO DTIC

EACH ACTIVITY IS RESPONSIBLE FOR DESTRUCTION OF THIS DOCUMENT ACCORDING TO APPLICABLE REGULATIONS.

UNCLASSIFIED/~~LIMITED~~

U.S. GOVERNMENT PRINTING OFFICE : 1993 O - 150-524

UNANNOUNCED

PHOTOGRAPH THIS SHEET

AD-B967 060

DTIC ACCESSION NUMBER

LEVEL

INVENTORY

1

TCIR 636

DOCUMENT IDENTIFICATION

26 Feb 1951

Distribution auth to DOD and DOD contractors only; specific authority; (22 Dec 89). Other requests shall be referred to Commander, Chemical Research, Development and Engineering Center, ATTN: SMCCR-SPS-T, Aberdeen Proving Ground, MD 21010-5423.

DISTRIBUTION STATEMENT

ACCESSION FOR	
NTIS GRA&I	☐
DTIC TAB	☐
UNANNOUNCED	☒
JUSTIFICATION	per ltr
BY	
DISTRIBUTION	
AVAILABILITY CODES	
DIST	AVAIL AND/OR SPECIAL
D-16	

DISTRIBUTION STAMP

QUALITY INSPECTED

DTIC ELECTE DEC 27 1989 S E D

DATE ACCESSIONED

DATE RETURNED

89 12 26 241

DATE RECEIVED IN DTIC

REGISTERED OR CERTIFIED NO

PHOTOGRAPH THIS SHEET AND RETURN TO DTIC-FDAC

DTIC FORM 70A MAR 86

DOCUMENT PROCESSING SHEET

PREVIOUS EDITIONS MAY BE USED UNTIL STOCK IS EXHAUSTED.

TCIR 636
Copy-1

~~CONFIDENTIAL~~
[redacted]

L

C

1 9 1951

UNCLASSIFIED

TCIR 636

Project 4-08-03-005

AD-B967 060

TECHNICAL COMMAND INTERIM REPORT

THE PREPARATION OF METHANEPHOSPHONYL CHLOROFLUORIDE

by

F. W. Hoffman

Regraded UNCLASSIFIED
by authority of Chief
[illegible]
by CORNELIA [illegible]
Classified Do[illegible]
CW LABS, A Cml C, Md.
JAN 26 [illegible]

CANCELLED
REVIEWED FOR CLASSIFI[illegible]
OCT [illegible]
(Date)
N/C

Regraded ~~CONFIDENTIAL~~
by ~~authority of CO, CMLC~~
CML & RAD LABS, A Cml C, Md.
by
Member Classified Documents Review Committee
NOV 18 1954

CHEMICAL DIVISION
TECHNICAL COMMAND
ARMY CHEMICAL CENTER, MARYLAND

26 February 1951

UNCLASSIFIED

Copy 1

~~CONFIDENTIAL~~ [redacted]

[redacted]

TL-56-5-67

TL-S(54)166

~~CONFIDENTIAL~~ CANCELLED

[redacted]

19 1951

UNCLASSIFIED

CHEMICAL DIVISION
TECHNICAL COMMAND
ARMY CHEMICAL CENTER, MARYLAND

TECHNICAL COMMAND INTERIM REPORT

This is an unedited report. It is issued to transmit urgently needed data to authorized personnel as rapidly as possible. Its conclusions are tentative and are subject to revision.

TCIR 636
Project 4-08-03-005

THE PREPARATION OF METHANEPHOSPHONYL CHLOROFLUORIDE

Regraded ~~CONFIDENTIAL~~ CANCELLED
by authority of CO, CMLC
CML & RAD LABS, A Cml C, Md.
by L. G. Walker 2/Lt
Member Classified Documents Review Committee
NOV 18 1954

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C., sections 793 and 794. The transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

UNCLASSIFIED

~~CONFIDENTIAL~~ CANCELLED

[redacted]

[redacted]

UNCLASSIFIED

~~CONFIDENTIAL~~ CANCELLED

[redacted]

TCIR 636
Project: 4-08-03-005

THE PREPARATION OF METHANEPHOSPHONYL CHLOROFLUORIDE

I. OBJECT.

The work reported herein was undertaken under Project 4-08-03-005, Agents of the G Series, in connection with an investigation of the mechanism of the fifth step of the GB synthesis. This involved, among other things, a study of the formation and properties of methanephosphonyl chlorofluoride which might be a possible intermediate in the GB synthesis.

II. HISTORICAL.

The mechanism of the fifth step of the GB synthesis proposed by the German investigators in which the dichloride of the di-di mixture reacts with isopropanol with formation of chloro-GB, simultaneously with the reaction of the difluoride and isopropanol with formation of GB and HF, with the latter product converting the chloro-GB to GB, seems doubtful since it has been reported that the rate of reaction of difluoride with isopropanol is extremely slow. Among the possible postulations of various types of mechanisms of the fifth step are two which involve the intermediate formation of methanephosphonyl chlorofluoride. The following two sequences of equations may serve to illustrate the postulated mechanisms:

1.a. $CH_3POCl_2 + (CH_3)_2CHOH \longrightarrow CH_3PO(Cl)OCH(CH_3)_2 + HCl$

b. $CH_3PO(Cl)OCH(CH_3)_2 + CH_3POF_2 \longrightarrow CH_3PO(F)OCH(CH_3)_2 + CH_3POClF$

c. $CH_3POClF + (CH_3)_2CHOH \longrightarrow CH_3PO(F)OCH(CH_3)_2 + HCl$

2.a. $CH_3POCl_2 + CH_3POF_2 \rightleftarrows 2CH_3POClF$

b. $CH_3POClF + (CH_3)_2CHOH \longrightarrow CH_3PO(F)OCH(CH_3)_2 + HCl$

CANCELLED ~~CONFIDENTIAL~~

[redacted]

UNCLASSIFIED

Because of these considerations, it was of interest to investigate the synthesis of the hypothetical intermediate CH_3POClF, and to determine its chemical and physical properties. However, it was realized that its synthesis and its reaction with isopropanol, according to equation 2, would by no means prove that the fifth step actually involves its intermediate formation according to either one of the two possibilities outlined above, but would indicate the possibilities of its being an intermediate in the fifth step reactions.

III. EXPERIMENTAL.

The methanephosphonyl dichloride, difluoride, and GB used in this work was obtained from the Pilot Plant of the Plants Division or Process Laboratory of the Chemical Division.

A. Preparation of Methanephosphonyl Chlorofluoride.

Plant GB was heated in a 3-l. round-bottom flask, equipped with a reflux condenser surmounted by a glass tube extending directly into the exhaust tract. The pot temperature rose to 160° at which point gas evolution began. The temperature then dropped to 145°, remained constant as long as gas was evolved, and finally began to rise gradually. At 180° the heating was stopped and the slightly yellow-brown colored residue of crude methanefluorophosphonic acid cooled to room temperature for further reaction with thionyl chloride.

To 438.5 g. of crude methanefluorophosphonic acid was added 500 g. of thionyl chloride (c.p.) in one portion and the mixture refluxed for 6 hours until the temperature rose to 80°. Another 50 g. of thionyl chloride was then added and the mixture heated for another 3 hours during which the pot temperature finally reached 127°. Distillation of the reaction product through a 15 cm. column packed with helices at 68 mm. pressure yielded 389 g. of crude chlorofluoride boiling at 52-67°. The product was redistilled through a 30 cm., helix-packed column, to yield 240 g. of a constantly boiling fraction at 41° and 30 mm. pressure.

Determination of ionic fluorine:

For CH_3POClF calc. 0%; found, 1.77%

Based on this analysis the product contains 9.3% of methanephosphonyl difluoride, if the ionic fluorine is calculated as such.

The distillate was solidified by cooling with a dry ice-acetone bath and slowly thawed. The part which was liquid at -23° was filtered from the crystal sludge, and the cut of the filter residue melting at -23° to -19° separated by filtration. The residue melting above -19° was discarded. Determination of ionic fluorine in the fraction melting at -23° to -19° showed a content of 1.56% F^-. Since fractional crystallization did not lower the difluoride content markedly, 190 g. of the recrystallized product was redistilled through the 30 cm. column giving 127 g. of distillate at 34-35° and 14 mm. pressure.

Determination of ionic fluorine: found 0.5%.

The content of 0.5% F^- corresponds to 2.7% of methanephosphonyl difluoride.

Analysis of another sample of chlorofluoride prepared as described above, but purified only by repeated distillation under reduced pressure, gave the following values:

CH_3POClF	Calculated	Found
Cl	30.44	30.45
Total F	16.31	16.47
Ionic F	0	0.87

Yields of 72-82% of crude CH_3POClF, b.p. 120-144°, were obtained in a large number of various runs. The boiling point at atmospheric pressure of the pure compound is 126.0-126.5°.

B. Determination of Disproportionation of Methanephosphonyl Chlorofluoride.

Samples of approximately 0.40 g. of methanephosphonyl chlorofluoride having an ionic fluorine content of 0.83% were bulbed, weighed, and kept in a thermostat at 60 ± 0.5° for various periods of time. The samples, removed from the thermostat, were cooled in ice water and immediately titrated for ionic fluorine. The obtained values are listed in Table 1 in column 3. Column 4 gives the percentages of difluoride present in the product as calculated from the values in column 3.

Table 1

Analysis of Samples of Methanephosphonyl Chlorofluoride

1 Sample No.	2 Time hr.	3 Ionic F %	4 Difluoride %
1	0	0.83	4.37
2	3.25	1.63	8.58
3	20.25	1.78	9.37
4	48.5	1.87	9.84
5	70	2.11	11.11

C. Purification of Methanephosphonyl Difluoride.

Methanephosphonyl difluoride obtained from the Pilot Plant was distilled through 40 cm., helix packed column, of 12 mm. diameter. The fraction boiling at 98-98.5° was stirred at room temperature for 24 hours with 5% by weight of dry, powdered sodium fluoride. The difluoride was then distilled at low pressure without removing the NaF, in order to avoid exposure to the atmosphere, and without applying heat to the distillation flask. The difluoride was condensed in a receiver by cooling with dry ice acetone. Determination of ionic fluorine and acidity proved it to be purer than any other sample of difluoride purified in different manner.

Analysis:	Calculated %	Found %
Ionic F	18.99	19.16
Acidity (calc. as CH_3POF_2)	100	100.18

D. Determination of Ionic Fluorine in Pure Di-Di Mixture.

The methanephosphonyl dichloride used in this run was purified by fractionation through a 40 cm., helix packed heated column, at a reflux ratio of 10:1. A cut, constantly boiling at 160°, was collected as pure dichloride.

An equimolar mixture of pure methanephosphonyl dichloride and difluoride was prepared and its content of ionic fluorine determined over a period of 96 hours at room temperature. The values obtained are listed in Table 2.

Table 2

Analysis of Samples of Di-Di Mixture

Time hr.	Ionic F %
1	9.37
4	9.32
24	9.34
96	9.02

IV. DISCUSSION.

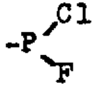
Methanephosphonyl chlorofluoride can easily be prepared in fair yields by chlorination of methanefluorophosphonic acid with thionyl chloride under reflux. Yields of 80% of crude chlorofluoride have been obtained frequently.

It has been observed that the chlorofluoride has a pronounced tendency to disproportionate according to the equation,

$$2CH_3POClF \longrightarrow CH_3POCl_2 + CH_3POF_2$$

into dichloride and difluoride when refluxed at atmospheric pressure. This makes it impossible to fractionate the chlorofluoride through long columns at atmospheric pressure. It is advisable to use short columns not longer than 15 cm., and carry out the fractionation under reduced pressure. A product purified in this manner will always contain a small percentage of difluoride. The purest product obtained during this work had a difluoride content of 2.7% and was sufficiently pure for further reactions.

The disproportionation of the chlorofluoride at 60° was followed over a period of 70 hours by determination of the ionic fluorine content. Under the conditions of the analysis the P-F linkage in the chlorofluoride is stable towards hydrolysis, behaving like the second P-F linkage in the difluoride. Hence, any disproportionation to difluoride and dichloride will result in the formation of a hydrolyzable P-F bond, and can be followed by the increase of ionic fluorine in the chlorofluoride. The values in Table 1 show that over a period of 70 hours the ionic fluorine content increases 1.28%, corresponding to an increase of 6.74% in difluoride content.

The present pilot plant process for the production of di-di mixture consists in fluorination of methanephosphonyl dichloride with 1 mol of anhydrous HF; the resulting di-di mixture appears not to contain methanephosphonyl chlorofluoride. Since the chlorofluoride does not, or at least only to a small extent, disproportionate at the temperatures applied during the fluorination process, it must be assumed that the slow disproportionation is catalyzed by anhydrous HF, or that the fluorination of a  $-P{\overset{Cl}{\underset{F}{\langle}}}$ group takes place at a rate several orders of magnitude faster than that of a $-PCl_2$ grouping.

The first assumption that the disproportionation is catalyzed by HF finds a parallel in the fluorination of the much more resistant $-CCl_3$ and CHF_2 groups with anhydrous HF which has been investigated thoroughly by Whalley (J. Soc. Chem. Ind., 66, 427-430, 430-433 (1947); 67, 331-333 (1948)). Aliphatic compounds such as CH_3CCl_3, $CH_2Cl \cdot CCl_3$, $CH_3 \cdot CHCl_2$ etc. can be converted to the monofluorides under suitable conditions with HF (catalyzed by $SnCl_4$ or uncatalyzed) in good yields. If, however, the reaction is carried out with antimony pentachloride as catalyst no monofluoride is obtained, but fluorination proceeds to the di or trifluoride stage, respectively. Whalley concludes from his observations that in the polyfluorination the actual role of the antimony catalyst is twofold. First, it seems to act as a true catalyst and serves the purpose of homogenizing the immiscible halohydrocarbon and HF. Second, it provides a suitable medium for the disproportionation of the monofluoride according to the equation:

$$2RR'CClF \longrightarrow RR'CF_2 + RR'CCl_2$$

Drawing a parallel between the fluorination of $-PCl_2$ and $>CCl_2$ groupings, it is obvious that the former proceeds with extreme ease. Hence, it is possible that the disproportionation of $-PClF$ to $-PCl_2$ and $-PF_2$ does not require as active a catalyst as pentavalent antimony, but is effected by HF, the fluorinating agent itself.

The possibility of a reversibility of the disproportionation reaction of methanephosphonyl chlorofluoride is by no means excluded. Since the present pilot plant process for the di-di mixture consists in fluorination of methanephosphonyl chloride with one equivalent of anhydrous HF, an equilibrium formation of the chlorofluoride will result in a decrease of the ionic fluorine content below the theoretical value for the di-di mixture. Therefore, the values for ionic fluorine in a di-di mixture freshly prepared from the purified components were determined over a period of 96 hours. The values obtained are listed in Table 2. The change in ionic fluorine content during the first 24 hours is within the limits of experimental error. After 96 hours a decrease of 0.35% of F^- was observed corresponding to about 1% reaction according to

$$CH_3POF_2 + CH_3POCl_2 \longrightarrow 2CH_3POClF.$$

The only conclusion to be drawn from this result is the possibility of chlorofluoride formation to a small extent with the equilibrium almost exclusively in favor of the di-di mixture. This, however, does not exclude a mechanism of the fifth step as illustrated by equations 1 and 2. A determination of the rate of reaction of the fifth step might be helpful in eliminating the German mechanism and/or mechanisms 1 and 2 (see Historical section) from the list of theoretically possible routes. The overall rate of the German process would be determined by the slowest one of the three steps, all of which can be determined singly. The same consideration holds for the proposed mechanisms 1 and 2. Preliminary experiments indicate that reaction 1c(=2b) is rather rapid, whereas 1b is extremely slow, if it occurs at all; this leaves 1a as rate determining step. Mechanism 2 appears to be excluded due to the slow rate of step 2a as compared to the rapid formation of GB from the di-di mixture.

Since determinations of the rate of reaction of GB formation from di-di mixture by calorimetric measurements have been carried out, in the meantime, by Physical Branch and seem to indicate a higher order of reaction, further work in the indicated direction has been discontinued.

V. <u>SUMMARY</u>.

Methanephosphonyl chlorofluoride, b.p. 126.0-126.5°, b_{30} 41°, has been prepared in good yield by chlorination of crude fluorophosphonic acid with thionyl chloride, and its rate of disproportionation at 60° has been determined.

Two postulated mechanisms for the fifth step of the GB synthesis and the mechanism proposed by the German investigators appear to be improbable on account of the data obtained during this investigation.

[redacted]

TCIR 636

Project: 4-08-03-005

The Preparation of Methanephosphonyl Chlorofluoride.

Work Done:
  Started: 11 July 1949
  Completed: 2 June 1950
    (Intermittent)

Notebooks: 2951, 3046

Submitted by:

F. W. Hoffmann
*F. W. Hoffmann

Walter Gall / F.W.H.
Walter Gall

* Author

Approval Recommended by:

Merchant L Cushing
Merchant L. Cushing
Captain, Cml C
Chief, Organic Branch

APPROVED:

T H. Whitehead
T. H. WHITEHEAD
Lt Colonel, Cml C
Chief, Chemical Division

[redacted]

~~CONFIDENTIAL~~

[redacted] UNCLASSIFIED

CANCELLED

DISTRIBUTION LIST

Copies made: 16

Copy	1 - 5	Technical Library
	6	Chief Chemical Officer, Field Office, Army Chemical Center, Md., Attn: Research & Engineering Division
	7	Director, Biological Department, Camp Detrick, Frederick, Md.
	8	Chief, Medical Division, Bldg. 355, Army Chemical Center, Md.
	9 - 10	Canadian Liaison Officer, Army Chemical Center, Md. THRU: Research & Engineering Division (If not denied to foreign nationals)
	11 - 12	British Liaison Officer, Army Chemical Center, Md. THRU: Research & Engineering Division (If not denied to foreign nationals)
	13 - 14	Central Air Documents Office, Wright-Patterson Air Force Base, Dayton, Ohio, Attn: CADO-D (If not Top Secret or Restricted Data, Type A and B)
	15	President, Chemical Corps Board, Army Chemical Center, Md.
	16	Commanding Officer, Dugway Proving Ground, Tooele, Utah

LLED

~~CONFIDENTIAL~~

[redacted]

UNCLASSIFIED

UNCLASSIFIED/~~LIMITED~~

DEFENSE TECHNICAL INFORMATION CENTER
CAMERON STATION
ALEXANDRIA, VIRGINIA 22304-6145

OFFICIAL BUSINESS - PENALTY FOR PRIVATE USE, $300
POSTMASTER: DO NOT FORWARD

AD Number	Class	Pages	Type Copy	Source	Priority
B967060	U L	11	H	F	

Received Date: 06-APR-95 248

To : 21003
Requested By : PITT2503

ATTENTION : M P GARDNER

SCIENCE APPLICATIONS INTL CORP MCLEAN

PO BOX 1303
MCLEAN, VA 22102-3799

262669001

UNCLASSIFIED/~~LIMITED~~