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UNITED STATES ENGINEER OFFICE
MANHATTAN DISTRICT
OAK RIDGE, TENNESSEE

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2 January 1946.

Subject: Transmittal of Summary Report.

To: The District Engineer, Manhattan District, Oak Ridge,
Tennessee.

(Attention: Lt. Col. A. V. Peterson).

Inclosed are copies 11-25A of Report A-2704 entitled
"The Identification of the By-Products from the Reaction of Tuballoy
Trioxide with Hexachloropropene", submitted 14 December 1945. Copies
1 - 2A were retained by Col. G. J. Forney, copies 3 - 10A were sent to
TEC and copies 26 - 30A were retained by Dr. E. T. McBee.

C. E. Winters
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Incl.

Purdue Report A-2704
cys. 11 - 25A.

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A-2704

Summary Report

on

THE IDENTIFICATION OF THE BY-PRODUCTS FROM THE REACTION
OF TUBALLOY TRIOXIDE WITH HEXACHLOROPROPENE

Submitted

December 14, 1945

under

Contract No. W-7405 eng-74

by

Purdue Research Foundation

and

Department of Chemistry, Purdue University

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Summary Report

on

Research at Purdue University

by

Purdue Research Foundation and Department of Chemistry

December 14, 1945

THE IDENTIFICATION OF THE BY-PRODUCTS FROM THE REACTION OF
TUBALLOY TRIOXIDE WITH HEXACHLOROPROPENE

Abstract

Tuballoy tetrachloride may be prepared by the reaction of tuballoy trioxide with hexachloropropene.

The U.S. Army Engineer Corps requested that Purdue University determine the identity of the by-products from this reaction.

A reaction between tuballoy trioxide and hexachloropropene was carried out at the Oak Ridge, Tenn. plant operated by the Tennessee Eastman Corp. The tuballoy tetrachloride was filtered off and a portion of the filtrate was brought to Purdue University by Mr. E. L. Wagner.

The sample was carefully rectified at atmospheric pressure until the distillation temperature reached 180°C. and then the rectification was completed at reduced pressures.

The chlorine analyses and molecular weights were determined for certain fractions obtained by the rectification. From these data the material in each fraction was tentatively identified. Derivatives were made of the compounds for positive identification. Identification data for the compounds are listed in Table 1.

The first fraction obtained boiled at 75.0-75.3°C. and was identified by its analyses and refractive index as carbon tetrachloride. There was no indication of any material, such as phosgene, boiling below 75°C. The next fraction boiled at 119.4-120.0°C. The analyses for this material corresponded to the analyses for tetrachloroethylene and the material reacted with chlorine to give hexachloroethane. A third fraction was obtained boiling at 158.0-158.3°C. and the analyses for this material agreed very well with the theoretical values for trichloroacrylyl chloride. This material was further identified by converting a sample of it to trichloroacrylamide. A solid material was obtained in the fraction boiling

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Table 1

Physical Constants and Analytical Data for
Rectification Fractions

<u>Identity</u>	<u>B.R., °C.</u>	<u>Vol., %</u>	<u>Cl., %</u>	<u>Mol. Wt.</u>	<u>Derivative</u>
Fraction A	75.0-75.3	2.3-	92.9	154	Refr. Index
CCl ₄	76	---	92.9	154	
Fraction C	119.4-120.0	1.2	87.1	166	C ₂ Cl ₆
C ₂ Cl ₄	120	---	85.6	166	
Fraction EF	158.0-158.3	35.3	73.2	194	CCl ₂ =CClCONH ₂
CCl ₂ =CClCOCl	158	---	73.3	194	
Fraction HJ(s)	60-70/13 mm.	2.0	90.9	---	None
C ₂ Cl ₆	186	---	90.0	237	
Fraction LMO	99.0-93.0/15 mm.	36.8	83.0	257	None
C ₃ Cl ₈	92/15 mm.	---	85.6	249	
C ₄ Cl ₁₀	99/20 mm.	---	81.6	261	

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60-70°C./13 mm. Hg and was identified as hexachloroethane. A fifth fraction, boiling 88-93°C./15 mm. Hg, was not completely identified, but it was concluded from experimental work that this material was a mixture of hexachloropropene and hexachlorobutadiene.

A reaction between tuballoy trioxide and hexachloropropene was conducted at Purdue University in which all of the gaseous products boiling above liquid air temperatures were trapped and examined. A series of traps maintained at approximately 0°, -80° and -180°C., respectively, was used to collect the product.

The first trap, cooled by ice-water, contained a small amount of organic material. This was probably carbon tetrachloride which was carried over mechanically. The second trap, cooled by a dry ice-trichloroethylene mixture, contained about 1 ml. of chlorine dioxide. The last trap, cooled by liquid air, contained 2-3 ml. of hydrogen chloride.

With every addition of tuballoy trioxide, there was an intermittent passage of gases through a scrubber, which followed the liquid air trap. No carbon monoxide was detected in the effluent gases, however, so the gases which passed through the liquid air trap must have been oxygen or an insufficient amount of carbon monoxide to displace the air originally present in the system.

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THE IDENTIFICATION OF THE BY-PRODUCTS FROM THE REACTION OF
TUBALLOY TRIOXIDE WITH HEXACHLOROPROPENE

Hexachloropropene reacts readily with tuballoy trioxide in the liquid phase to give a good grade of tuballoy tetrachloride. The tuballoy tetrachloride may be filtered off, washed with carbon tetrachloride and used directly in the plant. The purpose of this work, however, was to determine the identity of the by-products of this reaction.

A 500 ml. sample of the filtrate from a reaction between tuballoy trioxide and hexachloropropene identified as HCP X-41 was brought to Purdue University by Mr. E. L. Wagner. The sample was obtained from a reaction carried out at the Tennessee Eastman Corp. plant at Oak Ridge, Tennessee and represented approximately 50% of the material from one experiment.

A part of the sample (350 ml.) was carefully rectified on a Hyper-Cal Podbielniak Column of 133 theoretical plates until the distillation temperature reached 180°C. The pot residue was then transferred to a 12-plate Lecky-Ewell column and the rectification was completed at a reduced pressure of 13-15 mm. of Hg. The rectification data are summarized in Table 1 and a plot of these data is shown in Figure 1.

The first distillate boiled at 75°C., indicating that there was substantially no low boiling material such as phosgene present. Approximately 2.3% by volume of the amount charged boiled at 75-75.3°C. (Fraction A). The distillation temperature then rose rather sharply to about 119°C. where a second small fraction was obtained (Fraction C). Again the distillation temperature rose rather sharply and a third fraction was obtained boiling at 158-158.3°C. (Fractions E and F). The latter fraction comprised approximately 35.3% by volume of the amount charged. It was evident from the variations in the distillation temperature that decomposition was occurring at about 180°C. (Fraction G), so the rectification was stopped. The still residue was transferred to a Lecky-Ewell column and the rectification completed at a pressure of 13-15 mm. Hg. The distillation temperature rose slowly from 52-88°C. at 13-15 mm. Hg. (Fractions H, J, and K) and no well defined fraction was obtained. A solid separated from the distillate which was collected at 55-70°C. at 13-14 mm. Hg. (Fractions I and J). The solid was filtered off and analyzed separately. When the distillation temperature reached 92°C. (end of Fraction M), the rectification was interrupted for one hour. When the rectification was resumed, the distillation temperature dropped to 80°C. and 7 ml. of distillate was removed (Fraction N) before the temperature returned to 92°C. The lower boiling material was presumably due to decomposition during the interruption and therefore Fraction N was not examined critically.

Chlorine analyses were made for all of the fractions except B and D and the molecular weight was determined for Fractions A, C, E^F, and LMO. These data and the theoretical values for proposed compounds are listed in Table 2.

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Table 1

Rectification Data for the Filtrate from HCP #41

<u>Fraction</u>	<u>Boiling Range, °C.</u>	<u>Pressure, mm. of Hg.</u>	<u>Volume, ml.</u>	<u>Volume, %</u>
A	75-75.3	Atmos.	8.3	2.3
B	75.3-119.4	"	5.0	1.4
C	119.4-120	"	4.3	1.2
D	120-158	"	5.4	1.5
E + F	158-158.3	"	123.3	35.3
G	158.3-180	"	3.2	0.9
H	52-67	13	5.5	1.6
J	67-72	14	4.6	1.3
K	72-88	15	20.4	5.8
L	88-90	14	34.0	9.7
M	90-92	15	28.0	8.0
N	80-92	15	7.0	2.0
O	92-93	15	67.0	19.1
Liq. res.	---		15.0	4.3
Trap	---		5.2	1.4
Total	---		336.2	95.8

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Table 2

Physical Constants and Analytical Data for RectificationFractions and Proposed Compounds

<u>Fraction</u>	<u>Boiling Range,</u> <u>°C.</u>	<u>Pressure,</u> <u>mm. Hg</u>	<u>Cl, %</u>	<u>Mol. Wt.</u>	<u>Proposed</u> <u>Compound</u>
A	75-75.3	atoms.	91.2	146	CCl ₄
A (purified)	---	"	92.9	154	CCl ₄
CCl ₄	76	"	92.9	154	---
C	119.4-120	"	87.1	166	CCl ₂ =CCl ₄
CCl ₂ =CCl ₂	120	"	85.6	166	---
E + F	158-158.3	"	73.2	194	CCl ₂ =CClCOC1
CCl ₂ =CClCOC1	158	"	73.3	194	---
G	158-180	"	80.1	---	---
H (s)	52-67	13	90.7	---	CCl ₃ CCl ₃
H (l)	52-67	13	85.2	---	mixture
J (s)	67-72	14	91.5	---	CCl ₃ CCl ₃
J (l)	67-72	14	85.0	---	mixture
C ₂ Cl ₆	---		90.0	237	---
K	72-88	15	83.9	---	mixture
L	88-90	14	83.0	---	---
M	90-92	15	82.9	---	---
N	80-92	15	82.5	---	---
O	92-93	15	82.9	---	---
LMO	88-93	15	83.0	257	C ₃ Cl ₆ + C ₄ Cl ₈
C ₃ Cl ₆	92-93	15	85.6	249	---
C ₄ Cl ₈	99	20	81.6	261	---

Fraction A (75.0-75.3°C.)

Fraction A boiled approximately in the range for carbon tetrachloride (76°C.), but it contained 91.2% Cl (theory for CCl_4 is 92.9% Cl) and had a molecular weight of 146 (theory for CCl_4 is 154). The material in Fraction A had a very disagreeable odor indicating that some impurity was present. In an attempt to purify the material, it was shaken with twice its volume of a 10% sodium hydroxide solution. It was insoluble and heavier than the aqueous layer. There was a slight diminution in the volume of the organic layer during this process and the aqueous layer became yellow. The aqueous layer was separated and neutralized with hydrochloric acid. It became colorless and a gas was evolved which had a mercaptan-like odor. An insoluble solid settled out during neutralization of the aqueous layer, but there was an insufficient amount for identification. The organic layer was clear. It was filtered through Drierite and again analyzed. The purified material contained 92.9% Cl and had a molecular weight of 154. These values are identical with the theoretical values for carbon tetrachloride. The refractive index of the material in Fraction A was taken as a further check on its identity. The reported value for carbon tetrachloride at 15°C. is 1.463. The value determined for the material in Fraction A was 1.459 at 25°C. If the correction value of 0.0004 per degree is applied to the determined value, the result is 1.463 at 15°C. These data are therefore sufficient to establish the identity of the material in Fraction A as carbon tetrachloride.

Fraction C (119.4-120°C.)

The boiling range for the material in Fraction C corresponds to trichloroacetyl chloride and tetrachloroethylene. The material in Fraction C contained 87.1% Cl (theory for CCl_3COCl is 78.0% Cl and for $\text{CCl}_2=\text{CCl}_2$ is 85.6% Cl) and had a molecular weight of 166 (theory for CCl_3COCl is 182 and for $\text{CCl}_2=\text{CCl}_2$ is 166). The analytical values for the material in Fraction C correspond more closely to the values for tetrachloroethylene than to the values for trichloroacetyl chloride. However, since it was reported by E. L. Wagner that this material was believed to be trichloroacetyl chloride, attempts were made to prepare trichloroacetic acid through the reaction of the material in Fraction C with water and base and trichloroacetamide by reaction with aqueous ammonia. No reaction occurred in any case. The material had an unpleasant odor, so it was shaken with three times its volume of 10% sodium hydroxide. It was insoluble and heavier than the aqueous layer and there was no apparent diminution in volume. The organic layer was separated and dried with Drierite. Approximately one-half of the material was placed in a small tube exposed to a 200-watt light bulb and chlorine was bubbled through slowly for three to five minutes. The whole mass set to a white solid. The solid was removed and found to melt at 178-183°C. After recrystallization from methanol, it melted at 182°C. (uncorrected) in a sealed tube. The melting point of hexachloroethane is 185°C. These data are therefore sufficient proof that the material in Fraction C was tetrachloroethylene.

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Fraction E + F (158.0-158.3°C.)

This material was the major product, comprising about 35% of the total. It boiled in the range for trichloroacrylyl chloride, contained 73.2% Cl (theory for $\text{CCl}_2=\text{CClCOCl}$ is 73.3% Cl) and had a molecular weight of 194 (theory for $\text{CCl}_2=\text{CClCOCl}$ is 194). These data show very good agreement between the observed values for the material in Fraction E + F and the theoretical values for trichloroacrylyl chloride. Accordingly, a small amount of Fraction E + F was poured into concentrated aqueous ammonia and the white precipitate which was formed was filtered off. After recrystallization from water, it melted at 96.5-97.5°C. The melting point for the amide of trichloroacrylic acid is 96-97°C. The anilide of the material in Fraction E + F was also prepared, but the melting point for this compound was not found in the literature. These data are sufficient, however, to establish the identity of this fraction as trichloroacrylyl chloride.

Fraction G (158-130°C.)

This material is an intermediate fraction between Fractions T and H. The rectification curve shows that it boils over a 22° range and the chlorine percentage is intermediate between the percentages for Fractions F and H. Therefore, no attempt was made to identify this material.

Fractions H and J (52-72°C./15-14 mm. Hg)

Both of these fractions formed two phases, a solid and a liquid phase. The solid was removed from each by filtration and found to be insoluble in sodium hydroxide, hydrochloric acid and concentrated sulfuric acid, but soluble in acetone. It was recrystallized from methanol. The chlorine analyses on the two solids differed slightly (90.7% Cl and 91.5% Cl), but both of the recrystallized products melted sharply at 185°C. The melting points, boiling points and chlorine percentages indicate that the solid phases from both fractions are hexachloroethane. The sublimation temperature of hexachloroethane is 186°C.

No attempt was made to identify the liquid portions of these two fractions because it was assumed that they were solutions of hexachloroethane in the higher boiling fractions.

Fraction K (72-88°C./15 mm. Hg)

Fraction K is composed of intermediate material. The chlorine analysis of this material (83.9%) indicates that it contains mainly the same material present in Fractions L, M and O (83.0% Cl) with a small amount of a more highly chlorinated compound, probably hexachloroethane. No attempt was made to identify this material.

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Fractions L, M and O (88-93°C./15 mm. Hg)

Since the material in these fractions all boiled in the same range and contained substantially the same percentage chlorine (82.9-83.0% Cl), they were mixed and the identification work was made on the combined fraction. It was believed at first that this material was unreacted hexachloropropene. However, it is stated in the literature (2) that hexachloropropene boils at 99°C./15 mm. Therefore, a 150-ml. aliquot of the hexachloropropene used in the experiment from which this filtrate was obtained was rectified to determine the boiling range. The rectification was conducted at 15 mm. Hg pressure. The rectification data and the analytical data for the fractions are given in Table 3. These data show that about 23% of the starting materials boils below 91°C./15 mm., about 72% boils at 91-92°C./15 mm. and little or no material boils above 92°C./15 mm. Thus, it seems very likely that the value given in the literature for the boiling point of hexachloropropene at 15 mm. Hg pressure is in error. An analysis on the material boiling 91-92°C./15 mm. showed it to contain 87.3% Cl. This value is higher than the theoretical value (85.6% Cl) for hexachloropropene, but the analysis of the material from Fraction LMO contained only 83.0% Cl. Thus, it seems very likely that hexachloropropene boils about 92°C./15 mm., but the material obtained in Fraction LMO boiling at this temperature was not hexachloropropene.

Several tests were made with the material from Fraction LMO and these are presented below.

1. About 5 ml. was put in a glass tube which was illuminated by a 200-watt bulb and chlorine was passed through for 30 minutes. No apparent reaction occurred.
2. About 5 ml. was sealed in a glass tube with an equal volume of liquid chlorine and exposed to a 200-watt bulb for two hours. No apparent reaction occurred.
3. Twelve and one-half grams was mixed with one hundred grams of 10% sodium hydroxide and refluxed for four hours. No apparent reaction occurred.
4. Fifteen milliliters was mixed with 50 ml. of concentrated sulfuric acid and stirred at 50°C. for two hours, then cooled and poured onto ice. Only a very small amount of solid was obtained. A second experiment was conducted in a similar manner, except that it was heated for 60 hours at 90°C. Again only a small amount of solid was obtained. The combined solids from these two experiments were filtered off and partially dissolved in sodium hydroxide. Acidification of the aqueous layer gave a brown precipitate, but the quantity was too small to identify.
5. A small portion was treated with an acetone solution of potassium permanganate and found to be very unsaturated.

Table 3

Rectification Data for Hexachloropropene

<u>Fraction</u>	<u>Boiling Range,</u> <u>°C.</u>	<u>Volume, ml.</u>	<u>Volume, %</u>	<u>Cl, %</u>
A	33-75	0.1	0.0	---
B	75-85	2.0	1.3	86.4
C	85-91	33.0	21.6	86.4
D	91-92	110.0	71.9	87.3
Residue	---	8.0	5.2	85.2
Total		153.1	100.0	

6. The boiling point was taken with a small distilling flask equipped with a Vigreux column and found to be 208-209°C. There was a great deal of decomposition on heating.

7. The refractive index was 1.548 at 25°C. Heilbron (2) lists the refractive index of hexachloropropene as 1.5091 at 20°C. This discrepancy is so large that values for several different samples of hexachloropropene were determined. The starting material for this experiment had a refractive index of 1.548 and a sample of hexachloropropene from another source had a value of 1.546 at 25°C. Since these values all agreed so well and differed so much from the reported value, the molecular refractivity was calculated as follows:

$$6 \text{ Cl} = 6 \times 6.0 = 36.0$$

$$3 \text{ C} = 3 \times 2.5 = 7.5$$

$$1 \text{ C=C} = 1 \times 1.7 = 1.7$$

$$\text{Mol. ref.} = 45.2$$

The molecular refractivities were calculated from the Lorentz equation for refractive indices of 1.509 and 1.548 as follows:

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{\text{M.W.}}{D} = \text{MK}_D$$

$$n = 1.509$$

$$n = 1.548$$

$$\frac{1.3 \times 249}{4.3 \times 1.765} = 42.7$$

$$\frac{1.4 \times 249}{4.4 \times 1.765} = 44.8$$

These calculations show that the molecular refractivity calculated from a refractive index of 1.548 agrees much better with the molecular refractivity obtained from the sum of the atomic refractivities than a refractive index of 1.509. It seems likely, therefore, that the refractive index of hexachloropropene at 25°C. is approximately 1.55.

8. Following the directions given by Boeseken and Dujardin (1) for the hydrolysis of hexachloropropene to trichloroacrylic acid with sulfuric acid, two unsuccessful attempts were made to hydrolyze the material in Fraction LMO. The same conditions were used to hydrolyze a portion of Fraction D from the rectification of the starting material for this experiment. A brown precipitate was obtained. After recrystallization from carbon disulfide, a white solid was obtained which melted at 74-75°C. and contained 60.8% Cl. Trichloroacrylic acid melts at 76°C. and contains 60.6% Cl. These data show that the hexachloropropene used as a starting material for this experiment was hydrolyzed to trichloroacrylic acid while the material in Fraction LMO could not be hydrolyzed under identical conditions. The material in Fraction LMO is, therefore, of different composition

than the starting material. It is possible, however, that the material in Fraction LMO contains some hexachloropropene which did not hydrolyze because of the other material present. Also, any trichloroacrylic acid formed from the hexachloropropene in Fraction LMO might have been too soluble in the highly chlorinated material present in Fraction LMO to precipitate from solution.

9. The freezing range was determined as -26 to -20°C . Hexachlorobutadiene melts at -21°C ., but the melting point of hexachloropropene could not be found in the literature.

10. Approximately 5 ml. of the material from Fraction LMO was heated over an open flame in a Pyrex tube with about 1 g. of tuballoy trioxide. The reaction was sluggish, but after about 10 minutes of heating, some green solid was formed. A similar experiment was conducted using hexachlorobutadiene instead of hexachloropropene, but no reaction occurred.

In order to establish the identity of LMO definitely, it will be necessary to prepare a sample of pure hexachloropropene to compare its physical properties with those of Fraction LMO. Also, it will be necessary to examine the products of the reaction between the pure hexachloropropene and tuballoy trioxide. Pure hexachloropropene may be prepared by the condensation of chloroform with tetrachloroethylene in the presence of aluminum chloride.

In conclusion it may be stated that Fraction LMO is believed to be a mixture of hexachloropropene and hexachlorobutadiene. This assumption is based on the following facts:

1. The chlorine analysis for the material in Fraction LMO is intermediate between the theoretical values for hexachloropropene and hexachlorobutadiene.
2. The molecular weight determination for the material in Fraction LMO is intermediate between the theoretical values for both compounds.
3. The boiling point of the material in Fraction LMO corresponds to the boiling point of both hexachloropropene and hexachlorobutadiene.
4. The reaction of Fraction LMO with tuballoy trioxide is slow, but positive, indicating some nonreactive diluent is present in the hexachloropropene.
5. The refractive index of the material in Fraction LMO is intermediate between the values for hexachloropropene and hexachlorobutadiene.
6. Hexachloropropene is made commercially from technical propane. Technical propane contains some butane which may have been converted to hexachlorobutadiene.

Residues

The liquid residue was dark brown and was probably a solution of some of the solid residue in hexachloropropene. It was not analyzed.

The solid residue was dark brown. It was partially soluble in dilute hydrochloric acid to give a green solution. This was probably a solution of some tuballoy tetrachloride which was not removed in the filtration of the initial reaction mixture. The greater portion of the solid residue was insoluble in acid or base, but readily soluble in acetone. It was probably polymerized material.

Gaseous Products

The gaseous products are defined as that material which passes through a water-cooled condenser during the reaction of hexachloropropene with tuballoy trioxide. In order to determine the identity of these products, a reaction was carried out in which all products boiling above liquid air temperatures were trapped. A three-liter, three-neck flask was equipped with a water-cooled condenser, thermometer, mercury-sealed, motor-driven stirrer and an inlet for adding solid tuballoy trioxide intermittently. The inlet tube was closed at the end so that all gases passed through an outlet system connected to the top of the condenser. This outlet passed through a series of four traps, the first cooled by ice water, the second and third by a dry ice-trichloroethylene mixture and the fourth by liquid air. The exit from the liquid air passed through a small sulfuric acid bubbler into an ammoniacal solution of cuprous chloride. The purpose of the system after the liquid air trap was to detect carbon monoxide. If any carbon monoxide passed through the system, it would be absorbed in the ammoniacal solution and thus a comparison of the rate of passage of the gases through the sulfuric acid bubbler and the ammoniacal cuprous chloride solution would indicate the presence or absence of this gas in the effluent gases.

Eight hundred and twenty-one and four-tenths grams (5.50 moles) of hexachloropropene was added to the flask and heated to 160°C. by a Glascol heater. Small portions of tuballoy trioxide were added intermittently over a two-hour period until 159.0 g. (0.556 moles) had been added. The temperature was maintained at 160-180°C. during most of the experiment, but towards the end it fell to 140°C.

After the reaction was completed, each trap was examined separately. The trap cooled by an ice-water mixture contained a few drops of a water-insoluble material. This was probably some carbon tetrachloride which was carried through the condenser. It was not identified.

The second trap, which was cooled by a dry ice-trichloroethylene mixture, contained about 1 ml. of a red-orange solid. It was found to boil at 10-14°C. It gave a clear, colorless solution in water with a small

insoluble layer. The water-insoluble material was not identified, but was probably some organic material carried through the first trap. The aqueous solution was very acid toward pH paper and gave a white precipitate with silver nitrate. This material is therefore either Cl_2O (b.p. $3.8^\circ\text{C}.$) or ClO_2 (b.p. $9.9^\circ\text{C}.$) and the boiling point indicates that it is probably ClO_2 .

There was no material in the third trap, which was also cooled by a dry ice-trichloroethylene mixture, but the fourth trap, which was cooled by liquid-air, contained 2-3 ml. of a white solid. This solid melted rapidly when the trap was removed from liquid air and distilled at -85 to $-80^\circ\text{C}.$ The vapors smelled like hydrogen chloride and gave a white smoke with ammonia. Hydrogen chloride boils at $-83.7^\circ\text{C}.$ The water solution was very acid toward pH paper and gave a positive test for chloride ion. This material was probably hydrogen chloride. It is presumably formed from some impurity in the hexachloropropene, possibly pentachloropropene.

There was a passage of gases through the sulfuric acid bubbler with each addition of tuballoy trioxide, but the passage of gases through the ammoniacal cuprous chloride solution was equally vigorous indicating that no carbon monoxide was being absorbed. However, the fact that there was an intermittent passage of gases through the liquid air trap during the entire experiment indicates the formation of some gas which boils below liquid air temperature. This may have been oxygen or an insufficient amount of carbon monoxide to displace the air originally in the system.

It has been shown that the gaseous products from the reaction between technical hexachloropropene and tuballoy trioxide are chlorine dioxide, hydrogen chloride, some organic material which is mechanically carried over and either oxygen or a small amount of carbon monoxide. However, the total volume of gases per mole of tuballoy trioxide is probably only about three liters.

Table 4 lists the possible gaseous products from the reaction between hexachloropropene and tuballoy trioxide, some physical constants of these compounds and the trap in which they would have been found.

Miscellaneous

The tuballoy tetrachloride from the reaction described above was filtered off and the filtrate rectified. The rectification data are summarized in Table 5 and a plot of these data is shown in Figure 2. These data are submitted because they show different percentages of the various fractions. A 6:1 mole ratio of hexachloropropene to tuballoy trioxide was used in this reaction. This is the same ratio as was reported to have been used in the experiment at the plant.

The material boiling below $74^\circ\text{C}.$ in the experiment conducted at Purdue is probably acetone which was used to clean out the equipment and

Table 4
Possible Gaseous Products from the Reaction between
Tuballoy Trioxide and Hexachloropropene

<u>Compound</u>	<u>M.P., °C.</u>	<u>B.P., °C.</u>	<u>Color</u>	<u>Trap No.</u>	<u>Remarks</u>
H ₂ O	0	100	Colorless	1	Not found
Cl ₂ O	-20	3.8	Red-brown	1, 2	Possible
CCl ₄	-23	77	Colorless	1	Possible
CO ₂	---	-78	Colorless	4	Not found
ClO ₂	-59	10	Orange-red	1, 2	Found
Cl ₂	-102	-34	Green-yellow	2, 3	Not found
HCl	-112	-84	Colorless	4	Found
COCl ₂	-118	8	---	1, 2	Not found
CO	-207	-197	Colorless	---	Possible
O ₂	-218	-183	Colorless	---	Possible

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Table 5

Rectification Data for the By-Products from the Reaction
between Tuballoy Trioxide and Hexachloropropene

<u>Fraction</u>	<u>Boiling Range,</u> <u>°C.</u>	<u>Pressure,</u> <u>mm. Hg</u>	<u>Volume,</u> <u>ml.</u>	<u>Volume,</u> <u>%</u>	<u>Previous Expt</u> <u>Volume, %</u>
A	54-74	Atmos.	3	0.8	---
B	74-76	"	14	3.8	2.3
C	76-117	"	7	1.9	1.4
D	117-120	"	22	6.0	1.2
E	120-155	"	15	4.1	1.5
F	155-160	"	159	43.3	35.3
G	66-81	15	3	0.8	5.4
H	81-90	15	10	2.7	14.0
J	90-92	15	56	15.3	10.0
K	92-93	15	54	14.7	19.1
Res.	93	15	24	6.6	4.3
Total		--	367	100.0	94.5

the rectifying column. This fraction was not present in the previous rectification. The amount of carbon tetrachloride (Fraction B) is greater in the experiment conducted at Purdue and the amount of tetrachloroethylene (Fraction D) is much larger. The intermediate fractions (Fractions A, C and E) are larger in the experiment conducted at Purdue because the column used for the rectification was less efficient. Trichloroacrylyl chloride (Fraction F) is the main fraction from each experiment, but the percentage is greater in the one conducted at Purdue. The larger amount of trichloroacrylyl chloride and the smaller percentage of material boiling 81-93°C./15 mm. in the experiment conducted at Purdue probably indicate that the reaction conducted at Purdue made a more efficient utilization of the hexachloropropene. The amount of hexachloroethane, found in the fraction boiling 66-81/15 mm., was much smaller in the experiment conducted at Purdue. All of these data point to the fact that the minor constituents in the product depend on the conditions of the experiment and the reactants, and probably vary from one experiment to the next.

A calculation based on the data obtained from the experiment conducted at Purdue shows that 2.5 atoms of oxygen per mole of tuballoy trioxide are removed from the tuballoy trioxide by hexachloropropene to form trichloroacrylyl chloride. The remaining oxygen forms some chlorine dioxide and the rest presumably escapes as molecular oxygen.

Respectfully submitted,

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Project Leader

L. R. Evans
L. R. Evans

~~SECRET~~

Bibilography

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17 FIG-1

RECTIFICATION OF FILTRATE FROM HCP #41

Fig. 1

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Fig-2

RECTIFICATION OF FILTRATE FROM REACTION CONDUCTED AT PURDUE
BETWEEN TUBALLOY TRIOXIDE AND HEXACHLOROPROPENE.

Fig. 2

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