AECD-3965

0

CLINTON ENGINEER WORKS
TENNESSEE EASTMAN CORPORATION

Contract No. W-7401-eng-23

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States nor the Commission nor any person acting on behalf of the Commission makes any warranty or representation expressed or implied with respect to the accuracy, completeness, or usefulness of the information contained in this report or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights or

B Assumes any liabilities with respect to the use of or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above person acting on behalf of the Commission includes any employee or contractor of the Commission or employee of such contractor to the extent that such employee or contractor of the Commission or employee of such contractor prepares, disseminates or provides access to any information pursuant to his employment or contract with the Commission or his employment with such contractor.

Classification changed to U
by authority of Marion G. Buck 12/17/55
by H. Kiser date 12/1/11
and W. B. Borroughs date 12/1/11

THE REACTION OF

HEXACHLOROPROPYLENE WITH METALLIC OXIDES

This report was prepared as a scientific account of Government-sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission makes any warranty or representation expressed or implied with respect to the accuracy, completeness, or usefulness of the information contained in this report or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights or

B Assumes any liabilities with respect to the use of or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

ABSTRACT

Twenty-two metallic oxides were refluxed with hexachloropropylene. The anhydrous chlorides or other products formed are described for each oxide. The reactions were particularly vigorous with higher valent oxides of the fifth and sixth group elements.

Photostat Price \$ 1.80

Microfilm Price \$ 1.80

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

B. M. Pitt
E. L. Wagner
A. J. Miller

Submitted: January 14, 1946

68-1

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

-1-

THE REACTION OF
HEXACHLOROPROPYLENE WITH METALLIC OXIDES

INTRODUCTION

The success obtained in the chlorination of Tuballoy oxides with hexachloropropylene¹ led to the investigation of the action of this compound on other metallic oxides.

The reaction of TO_3 with hexachloropropylene, $\text{CCl}_2=\text{CCl}-\text{CCl}_3$ bp 210°C , had been previously found to go through the compounds TO_2Cl_2 and TCI_5 as 'intermediates'. The main organic by-product was tri-chloracrylyl chloride, $\text{CCl}_2=\text{CCl}-\text{COCl}$ bp 159°C , and the chlorine corresponding to the change in oxidation state from TO_3 to TCI_4 was accounted for² with the by-products CCl_4 , Cl_2Cl_4 , C_2Cl_6 , C_3Cl_8 , representing chlorinolysis of and chlorine addition to the excess hexachloropropylene. In addition to TO_3 the compounds T_3O_8 , $\text{TO}_4 \cdot 2\text{H}_2\text{O}$, TO_2Cl_2 , $\text{TO}_2(\text{NO}_3)_2$, and TO_2SO_4 had been chlorinated by this reagent with minor modifications in the procedure. TO_2 and $(\text{NH}_4)_2\text{T}_2\text{O}_7$ were found to be rather poor starting materials for this reaction.

The experiments described in this report were carried out by treating a large number of metallic oxides with hexachloropropylene according to a set procedure. The products of the reactions and conclusions relative to the activity of HCP with the various oxides are described.

SUMMARY

The action of refluxing hexachloropropylene was determined on twenty-two metallic oxides. It was found that anhydrous chlorides can

2

be prepared with exceptional ease from the higher valent metallic oxides of the fifth and sixth group elements.

EXPERIMENTAL METHODS

The experimental procedure followed in these survey experiments was to reflux the stated amounts of metal oxide and hexachloropropylene for the time given. The reaction mixture was allowed to cool to room temperature, and then filtered on a sintered glass funnel under a current of dry nitrogen. The solid product was washed free of organic matter with CCl_4 , and dried by vacuum or by suction on the funnel.

REACTIONS WITH HEXACHLOROPROPYLENE

<u>Oxide</u>	<u>Periodic Group</u>	<u>Wt. Oxide grams</u>	<u>HCP ml</u>	<u>Reflux Time Hours</u>	<u>Product</u>
CuO	I	10	100	3	No reaction
ZnO	II	10	100	3	Very slight reaction
CdO	II	15	100	1	55% converted to CdCl_2
HgO	II	15	100	1	Complete conversion to HgCl_2 which crystallized from the reagent on cooling
Al_2O_3	III	7.5	100	8	No reaction
CeO_2	III	10	100	4	No reaction
TiO_2	IV	10	100	2	Partial reaction with formation of soluble TiCl_4 . Bulk unreacted
ZrO_2	IV	20	100	4	No apparent reaction
SnO_2	IV	10	100	4	No apparent reaction
PbO_2	IV	15	100	5	Partial reaction with formation of PbCl_2
ThO_2	IV	20	100	5	Partial reaction
Cb_2O_5	V	15	100	2	Complete rapid conversion to CbCl_5 , completely soluble in the heated reaction mixture and in CCl_4 . Crystallized out in cooling

68-3

<u>Oxide</u>	<u>Periodic Group</u>	<u>Wt. Oxide grams</u>	<u>HCP ml</u>	<u>Reflux Time hours</u>	<u>Product</u>
V ₂ O ₅	V	5	100	--	Complete rapid conversion to VCl ₄ and VCl ₃ . VCl ₄ formed a solid solvate with the trichloroacetyl chloride.
		12	36	1	
Ta ₂ O ₅	V	10	100	4	Complete conversion to TaCl ₅ . Slower than with V ₂ O ₅ and Nb ₂ O ₅ .
CrO ₃	VI	5	100	1/2	Vigorous reaction forming CrCl ₃ .
Cr ₂ O ₃	VI	3	100	4	Slight reaction. Product contained 2% CrCl ₃ .
MnO ₃	VI	10	100	1/3	Reacted readily and completely with formation of MnCl ₅ which crystallized out on cooling the reaction mixture. A highly volatile metal chloride intermediate refluxed with the reagent during the reaction.
WO ₃	VI	6	100	1/4	Vigorous to WOCl ₄ .
		6	100	1	Mainly WCl ₆ . WCl ₅ or possibly a lower chloride may be final product.
TO ₃	VI	25	100	1/2	Readily chlorinated to fine crystalline TCl ₄ through soluble intermediate TCl ₅ .
T ₃ O ₈	VI	same as TO ₃			
TO ₂	VI	25	100	5	Very slight reaction over long period of time.
MnO ₂	VII	10	100	3	No reaction.
Fe ₂ O ₃	VIII	20	150	2	Reacted. Insoluble product 50% FeCl ₂ , 45% FeCl ₃ and 5% Fe ₂ O ₃ . Some FeCl ₂ in solution.
Co ₂ O ₃	VIII	20	100	3	Partial reaction. Product 50% CoCl ₂ and 50% Co ₂ O ₃ .
Ni(OH) ₂	VIII	10	100	2	No chlorination. Product NiO.
Ni ₂ O ₃	VIII	20	100	3	Slight reaction. Product 2% NiCl ₂ and 60% NiO.

4

DISCUSSION OF EXPERIMENTAL RESULTS

The work reported here was undertaken primarily as a survey, so that optimum conditions of technique, such as were determined for TO_3 , have not been investigated for each oxide. The two procedures which are most applicable to these reactions are:

1. Reflux the oxide with hexachloropropylene for a given time,

2. Continuously distill off the organic by-products as formed.

In collecting the data of this report only the reflux procedure was used. It seems evident that the distillation procedure would be preferably with many of the metal oxides. In the case of vanadium pentaoxide, which product VCl_4 forms a compound with trichloroacetyl chloride, the pure chloride would probably be obtained directly. Also when soluble chlorides are formed, as with CbCl_5 and TaCl_5 , distilling off the trichloroacetyl would be advantageous, since the halides are considerably more soluble in this compound than in the hexachloropropylene. In those reactions where mixtures of chlorides were obtained the distillation procedure would probably yield one compound, since the chlorination would be more complete. Also the higher temperatures attained would tend to produce the more stable chlorides. This would probably apply to the reaction with WO_3 where the reflux procedure yielded a mixture of WOCl_4 and WCl_6 . This reaction with WO_3 presents a very interesting case because of the various stable chloride and oxychloride intermediates which can be isolated.

Hexachloropropylene can be used for the rapid preparation of TiCl_4 , MoCl_5 , WCl_6 , WOCl_4 , CrCl_3 , CbCl_5 , TaCl_5 , VCl_3 and HgCl_2 . It will be noted that chlorination of the oxides of quinqué and sexavalent metals occurs with exceptional ease. The higher oxidation states apparently

5

favor the reaction, i.e. TO_3 , T_3O_8 , CrO_3 , etc. The lower oxides of these metals, TO_2 , Cr_2O_3 , on the other hand react only slightly under the conditions of the experiments.

The application of hexachloropropylene to the preparation of chlorides of other elements of group V is quite possible, although for the liquid products, a fractional distillation procedure would probably be necessary in order to obtain the pure compounds.

An analogous reaction with $\text{CCl}_2=\text{CCl}-\text{CF}_3$ and TO_3 yielded only a small amount of TF_4 . The reflux temperature was probably much too low because of the low boiling point of the compound, since in the vapor phase at 400°C this reagent gave a product consisting largely of TF_4 .

CONCLUSIONS

1. Hexachloropropylene can be used for the rapid preparation of the following oxides by the reflux method: TCl_4 , MOCl_5 , WCl_6 , WOCl_4 , CrCl_3 , CbCl_5 , TaCl_5 , VCl_3 and HgCl_2 .

2. The anhydrous chlorides can be prepared with exceptional ease from the higher valent metallic oxides of the fifth and sixth group elements.

References

- 1 CD-4106 - Wagner, Pitt, Dean, Miller
 C-2.350.1 - Wagner, Pitt, Curran, Schmitt, Miller
 C-2.350.3 - Pitt, Curran, Schmitt, Wagner, Miller
- 2 A-2704 - McBee, Evans