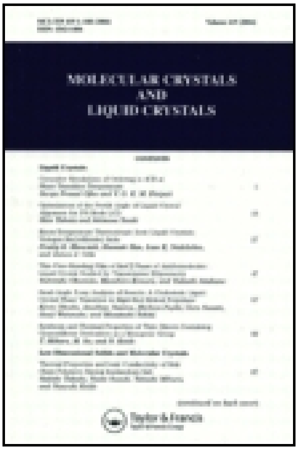

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THERMALLY-CONTROLLED FORMATION OF CRYSTALLINE HEXACHLOROBENZENE, HEXACHLOROETHANE, AND ANHYDROUS CHROMIUM CHLORIDE

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Abstract The high-temperature preparation of purple crystalline anhydrous chromium chloride ($CrCl_3$) by passing CCl_4 vapors over green Cr_2O_3 powder in an inert atmosphere is an instructive experiment in the inorganic chemistry laboratory. A systematic investigation of this synthesis (using a carefully calibrated tube furnace, X-ray powder diffraction, infra-red spectroscopy, and gas chromatography) revealed that the products formed as a consequence of the pyrolysis of CCl_4 are sensitive to the reaction temperature . When Cr_2O_3 is present, the formation of $CrCl_3$ dominates at temperatures between 600°C and 800°C; at temperatures above 900°C, C_6Cl_6 forms preferentially (presumably from the linking of the C-Cl free radicals produced by the pyrolysis) as the unreacted metal oxide is sintered to form eskolaite. In the absence of Cr_2O_3, the pyrolysis products are crystalline hexachloroethane (C_2Cl_6) at 600°C and needle-shaped crystals of hexachlorobenzene at temperatures above 900°C .

INTRODUCTION

The preparation of purple crystalline anhydrous chromium chloride by passing CCl_4 vapors over green Cr_2O_3 powder in a tube furnace has been well documented and, in fact, is an instructive experiment described in one of the more popular inorganic chemistry laboratory manuals.[1] However, the success of the synthesis is occasionally marred by an insignificant yield of the purple flakes accompanied by substantial amounts of other solid materials of various colors and crystalline forms. A systematic investigation of this synthesis with the objective of optimizing the yield of $CrCl_3$ and identifying the other crystalline materials using X-ray diffraction and infra-red spectroscopy was conducted.

The purpose of this communication is to report an unexpected result of this study: The same reactants and experimental set-up which result in the formation of the expected product, anhydrous chromium chloride, when run at one temperature, form a quintessential *aromatic organic compound*, hexachlorobenzene, when run at a different temperature.

EXPERIMENTAL CONDITIONS

Green chromium sesquioxide (Cr_2O_3) is dried and placed in a silica glass reaction tube (25 mm diameter x 90 cm length) and centered in a 46 cm-long tube furnace *inside a hood.* Nitrogen gas (99.998% pure), bubbled through heated CCl_4, carries CCl_4 vapors through the reaction tube past the Cr_2O_3 . The temperature, controlled by a variable voltage regulator, is measured by a built-in thermocouple connected to a pyrometer. The voltage settings and pyrometer readings were calibrated using an external chromel/alumel thermocouple whose accuracy had been verified by measuring the melting point of an aluminum brazing alloy (575°C). After repeating the synthesis 14 times under different conditions, the only significant variable seems to be the reaction temperature.

REACTION PRODUCTS

Four major crystalline materials were collected for identification. The yield and the location within the reaction tube where each of these materials formed was consistent for similar reaction conditions. For purposes of discussion, we refer to each product by its dominant color.

1. Purple: A variety of purple-colored products, in the form of flakes, powder, crystals, and a thin film coating on the inside wall of the reaction tube, formed when the temperature was between 600°C and 850°C. In general, the purple products were deposited within 12 cm of the (exit) end of the reaction tube.

2. Green: A green substance was produced during some of the syntheses carried out in the 700-826°C temperature range. It was found in small quantities as a coating on the walls of the reaction tube, approximately 1 to 2 cm long, in the same location as the purple product.

3. White : This product, which formed in significant quantities only at reaction temperatures above 900°C, was deposited as whiskers or filaments in the cooler portions near the end of the reaction tube. At temperatures between 800°C and 850°C both purple and white products formed.

4. Silver-gray: This shiny material was also produced only at reaction temperatures over 900°C. It was found in the part of the reaction tube that was in the central (hottest) portion of the furnace, precisely where the green chromium sesquioxide had been placed at the start of the reaction.

Identification of the solid products was attempted using infrared spectroscopy (Perkin-Elmer 783 Spectrophotometer, sample in KBr pellets) and X-ray powder diffraction [XRPD] (Philips PW 1700 Automated Powder Diffractometer with -325 mesh powder sample coated on glass slides). IR spectra were identified by comparison with either spectral data from the literature or the spectra obtained from samples of known materials. The diffraction data were analyzed using the diffractometer's matching program which is based on the Powder Diffraction File (PDF)[2] through 1989.

Purple: The X-ray diffraction data showed it to be essentially pure anhydrous $CrCl_3$ [PDF Card # 32-279] and the IR spectra of the product agreed in all respects with the spectrum of a commercial $CrCl_3$ sample. The optimum temperature for synthesizing anhydrous $CrCl_3$ was found to be 700-735°C. Under these conditions, the only product formed in significant quantities appears as purple flakes and crystals of $CrCl_3$; the average yield, based on the mass of chromium, is 57%.

White: This is unequivocally identified as hexachlorobenzene, C_6Cl_6, [PDF Card # 24-1760] with all but the 4 weakest lines of the standard pattern appearing in the observed pattern. Only six lines in the experimental XRPD pattern are not accounted for. The white compound grew as filaments in the end of the reaction tube where it was easy to collect them. Still, as there are other vapors in the reaction tube, the possibility of the filaments being contaminated with some other material cannot be ruled out. The IR spectrum matches that found in the literature for C_6Cl_6.[3] Also, the melting point of the white filaments was 229°C; the melting point of hexachlorobenzene is reported to be 231°C.[4]

The other two substances are not pure materials and the identification of their components is not complete.

Green: The XRPD matching program identified three components: eskolaite (78%), chromium oxide chloride, CrOCl (13%), and YN (9%). Eskolaite [PDF Card # 38-1479] is a mineral form of Cr_2O_3 (the starting material) and seems to form at high temperatures. CrOCl is prepared from a mixture of Cr_2O_3 and anhydrous $CrCl_3$ by the vapor transport method[5] [PDF Card # 28-371], and is a plausible product:

$$Cr_2O_3 + CrCl_3 \longrightarrow 3\ CrOCl$$

On the other hand, YN [PDF Card #10-221] is a most unlikely product. However, as is well known, the analytical properties of the powder diffraction method are limited to previously reported sets of d-spacings, in this case the data found in the Powder Diffraction File, and the d-spacings are a function of the unit cell dimensions of the sample. Since YN is face-centered cubic with $a \approx 4.9$ Å, we can surmise that the third component of the green powder has a similar unit cell, even though the compound has not been identified. The IR spectrum of this green sample has some peaks in common with that of Cr_2O_3;[6] other, considerably weaker, peaks were observed but could not be identified.

Silver-Gray: The XRPD matching program identified three components in this material too. The major component (45%) is eskolaite, as in the green product. The second component was identified as pentlandite (40%), an iron-nickel sulfide [PDF Card #30-657]; and the third substance was given as MnF_2 [PDF Card #1-0601] (15%). Given the nature of the reactants, neither of these two latter compounds is possible. However, hexachlorobenzene appears to be present in this material, since six of the seven strongest lines of C_6Cl_6 coincide with lines in this pattern. The matching program listed it as the third highest probability, but then rejected it based on a better overall match using the three components discussed above. Since our investigation has shown that white filaments of C_6Cl_6 form under the same conditions as does the silver-gray material, its presence in the silver-gray sample cannot be ruled out. On the other hand, the presence of another substance with a unit cell similar to that of MnF_2 can be ruled out since all but one of the peaks attributed to MnF_2 can be assigned to either eskolaite or C_6Cl_6. Since pentlandite is face-centered cubic with a = 10.038 Å, any substance with a similar Bravais lattice and unit cell dimensions would give a similar powder pattern. Interestingly, undecafluorocyclohexane (C_6HF_{11}) and dodecafluorocyclohexane (C_6F_{12}) have the same space group as pentlandite with a = 10.00 and 10.11 Å, respectively, while beta-(e,e,e,e,e,e)-1,2,3,4,5,6-hexachlorocyclohexane has a cubic cell with a = 10.08 Å, but is primitive rather than face centered.[7] Inasmuch as the formation of hexachlorobenzene has been proven, the possibility remains that this unidentified component is another organic chloride that has not been previously listed in the PDF.

We conclude that the silver-gray material contains unreacted Cr_2O_3 (as the high-temperature form eskolaite), hexachlorobenzene, and another, unidentified, material with a fcc unit cell ($a \approx 10$ Å).

Hexachloroethane

The role of Cr_2O_3 in the formation of C_6Cl_6 was considered. Would the reaction proceed in the absence of chromium oxide or is the chromium oxide necessary to catalyze the reaction ? To answer this question we passed CCl_4 through the tube furnace in the absence of

Cr_2O_3 and found that, at temperatures above 900°C, needle-shaped crystals of hexachlorobenzene, in significant yield, were formed in the reaction tube just past the end of the tube furnace. However, when the reaction was run at 600°C, a powdery white compound condensed near the end of the reaction tube. This material was identified as hexachloroethane (C_2Cl_6) on the basis of its camphor-like odor and the agreement between the IR spectra and gas chromatograms [HP Model 5890 Gas Chromatograph using a flame ionization detector on a non-polar column (30M HP1-Methylsilicone) at 150°C] of the white powder and a known sample of hexachloroethane. Since no trace of crystalline C_2Cl_6 [PDF Card # 11-841] appears in any of the XRPD data described above, we conclude that, when Cr_2O_3 is present, $CrCl_3$ forms in preference to C_2Cl_6.

CONCLUSIONS

At first glance it appears as if an "inorganic" reaction can be transformed, by a change in temperature, into the synthesis of a crystalline aromatic organic compound. In reality we are dealing with a much more complex situation wherein there are three competing sets of reactions: the high-temperature reaction of Cr_2O_3 and CCl_4 , the pyrolysis of CCl_4 (at different temperatures), and the effect of high-temperature sintering on green Cr_2O_3 powder.

On the basis of the above observations we can understand these reactions in terms of the competition between the various species present for the C-Cl free radical. If the pyrolysis of CCl_4 occurs at a location in the reaction tube wherein the C-Cl radical encounters Cr_2O_3 before it reacts with another C-Cl radical then $CrCl_3$ is formed. On the other hand, if it links up with another free radical first then C_6Cl_6 will form. At lower temperatures, other free radicals are formed (e.g., CCl_3) and C_2Cl_6 is the product in the absence of any competition from Cr_2O_3. Due to the large temperature gradient found in the tube furnace, the higher the temperature in the center, the more likely it is for significant amounts of C-Cl free radicals to form and react before they reach the Cr_2O_3 lying in the center of the tube. This is why C_6Cl_6 forms at high furnace temperatures.

The historical background (since 1845) of these reactions has been reported elsewhere.[8] Our "serendipitous" discovery of the formation of crystalline C_6Cl_6, in *significant* yields at high temperatures, led us into a detailed examination of the chemical literature as we tried to optimize the experimental conditions for the formation of both $CrCl_3$ and C_6Cl_6. Of more than passing interest is the fact that, in both the primary and secondary literature, the inorganic chemists have overlooked *all* references to the extensive pyrolysis studies by the organic chemists and the organic chemists (including Beilstein) have neglected to recognize the production of C_2Cl_6 and C_6Cl_6 by the inorganic chemists.

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