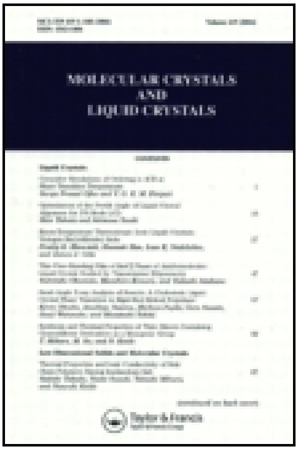

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Formation of Octachlorostyrene During the Synthesis of Chromium(Iii) Chloride

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FORMATION OF OCTACHLOROSTYRENE DURING THE SYNTHESIS OF CHROMIUM(III) CHLORIDE

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Octachlorostyrene has been recovered from the reaction tube, along with previously reported hexachlorobenzene, during the synthesis of $CrCl_3$ *from* Cr_2O_3 *and* CCl_4 *at high temperature. The region in the reaction tube where the octachlorostyrene was found, namely upstream from the* Cr_2O_3 *held at 890°C, suggests that this molecule is formed at a temperature below 890°C and that it decomposes if raised to that temperature. A low gas flow was used in this experiment, allowing products to diffuse countercurrently.*

Keywords: octachlorostyrene, synthesis, countercurrent formation

INTRODUCTION

Hexachlorobenzene and octachlorostyrene have attracted considerable attention recently because they have been detected in fish and water around areas where metals are produced [1–3]. The US Environmental Protection Agency's Office of Pollution Prevention and Toxics administers the Persistent Bioaccumulative and Toxic (PBT) Chemical Program [4]. Hexachlorobenzene and octachlorostyrene are two of several compounds for which the agency is developing national action plans. Other PBTs include PCBs, DDT, and alkyllead compounds. The presence of

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*Corresponding author. Fax: 509-323-5718; E-mail: cleary@ganzaga.edu octachlorostyrene in the environment is particularly interesting given that it is not manufactured commercially. Little is known about octachlorostyrene, but its similarity to hexachlorobenzene has led regulators to assume octachlorostyrene has toxic effects similar to hexachlorobenzene [5–7]. Our interest in these compounds comes from the unexpected observation of octachlorostyrene formation during the synthesis of chromium(III) chloride from chromium(III) oxide. We followed a modified procedure described by Angelici in his book ***Synthesis and Technique in Inorganic Chemistry*** [8]. Stevenson and Rudman reported in this journal a detailed study of the variety of products produced when processing chromium(III) oxide with CCl_4 at high temperature [9]. We observed essentially the same behavior reported by them, with the exception that we observed the formation of an additional product, octachlorostyrene, along with hexachlorobenzene. An important feature about this observation is where in the reaction tube the octachlorostyrene was observed. The purpose of this communication is to report our observation of the presence of octachlorostyrene when $CrCl_3$ is produced from Cr_2O_3 and CCl_4 at high temperature.

EXPERIMENTAL PROCEDURE

Synthesis

Chromium(III) oxide was prepared from ammonium dichromate by igniting a small pile (2.44 g, 9.67 mmol) of ammonium dichromate. The green fluffy oxide (chromium(III) oxide) was separated from the unreacted orange dichromate by washing with hot deionized water several times and filtering. The oxide was dried at 110°C for 30 min. The oxide was transferred to an open-ended quartz reaction tube which was inserted into a quartz flow tube. The flow tube was placed in a tube furnace and the system was purged with nitrogen gas. The nitrogen gas used in the purge was bubbled through a reservoir of carbon tetrachloride. The tube furnace was brought from room temperature to 890°C in 3 h. The N_2/CCl_4 purge was continued for 2 h. The furnace was then turned off and the sample allowed to cool while still under the N_2/CCl_4 gas flow. When the reaction tube had returned to room temperature, it was removed from the furnace. In addition to the expected formation of the desired product—$Cr^{III}Cl_3$ (purple crystals) downstream from the green oxide—colorless needle-shaped crystals formed at both ends of the reaction tube outside the furnace.

DSC Analysis

The melting point of the colorless needle-shaped crystals formed downstream was determined using a Perkin-Elmer DSC 7 differential scanning calorimeter. A sample of these needles (997 mg) was heated from 180°C to 245°C at 10°C/min.

GC/MS Analysis

The gas chromatographic/mass spectrometric (GC/MS) analysis was performed on a Hewlett-Packard 5890 Series II Plus gas chromatograph with a Hewlett-Packard 5972 Series mass selective detector. A 4 μL sample was heated from 60°C to 100°C at 20°C/min followed by heating at 30°C/min to 325°C. The column was 30 meters long with a 250 μm inside diameter and was coated on the inside with 0.25 μm of 5% crosslinked methylsilicone. A helium purge was used with a flow rate of 1.3 mL/min.

Single Crystal Structural Analysis

Crystals of octachlorostyrene were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream [10]. Data were collected at 203(2) K using a Bruker/Siemens SMART 1K instrument (Mo K_α radiation, $\lambda = 0.71073$ Å) equipped with a Siemens LT-2A low temperature device. Data were measured using omega scans of 0.3° per frame for 30 s, and a half sphere of data was collected. A total of 1471 frames were collected with a final resolution of 0.84 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART [11] software and refined using SAINTPlus [12] on all observed reflections. Data reduction and correction for Lp and decay was performed using the SAINTPlus software. Absorption corrections were applied using SADABS [13]. The structure was solved by direct methods and refined by least squares method on F^2 using SHELXTL [14]. The structure was solved in the space group P2(1)/c (#14) by analysis of systematic absences. All atoms are refined anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1.

RESULTS

The crystals recovered downstream from the furnace began melting at 226°C, and had a melting peak with a full width at half maximum of 0.75°C. The GC/MS analysis revealed this product to be essentially pure hexachlorobenzene. The GC/MS analysis, using the same parameters, of the crystals formed upstream of the furnace revealed a mixture of hexachlorobenzene and octachlorostyrene. The total ion chromatogram from

TABLE 1 Crystal Data and Structure Refinement for Octachlorostyrene

Compound	Octachlorostyrene
Formula (fw)	C_8Cl_8 (379.71)
T (K)	203(2)
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	$a = 7.5618(16)$ Å $b = 10.237(2)$ Å, $\beta = 93.323(4)°$ $c = 16.887(4)$ Å
V (Å^3), Z	1305.8(5), 4
D (calcd) (g cm^{-3})	1.931
Absorption coefficient (mm^{-1})	1.690
F(000)	736
Crystal size (mm)	$0.36 \times 0.06 \times 0.03$
θ range for data collection (deg)	2.33 to 25.00
Completeness to theta	94.1% (25.00°)
Index ranges	$-8 \leq h \leq 8$, $-12 \leq k \leq 10$, $-19 \leq l \leq 20$
Reflections collected	6632
Independent reflections	2159 [R(int) = 0.0467]
Absorption correction	Empirical
Max. and min. transmission	0.9511 and 0.5814
Data / restraints / parameters	2159 / 0 / 145
Goodness-of-fit on F^2	1.083
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0641, wR2 = 0.1471
R indices (all data)	R1 = 0.1097, wR2 = 0.1773
Largest diff. peak and hole	0.692 and −0.518 e.Å^{-3}

the upstream sample showed two peaks with retention times of 12.72 min and 13.90 min. The relative areas were 100(hexachlorobenzene) to 9.4(octachlorostyrene). The mass spectrum for each peak contained the parent ion (m/z = 284 for hexachlorobenzene and m/z = 380 for octachlorostyrene) expected for the given stoichiometry along with the required isotopic pattern for species containing such a number of chlorine atoms. A single crystal X-ray diffraction analysis of one of the crystals also confirmed it to be octachlorostyrene. The results of the crystal analysis are given in Table 1.

The observed space group and unit cell dimensions are consistent with the previously published single crystal data for octachlorostyrene, which was solved and refined in the non-standard setting of P2(1)/a [15].

DISCUSSION

Hexachlorobenzene has been observed previously during the synthesis of chromium(III) chloride from chromium(III) oxide [9]. In the present case, octachlorostyrene was also produced with hexachlorobenzene. Octachlorostyrene has been prepared previously by chlorination of a solution of 1,3-dichloro-2-vinylbenzene in CCl_4, following by addition of $SbCl_5$ [16]. It has also been prepared as a byproduct (20%) in the chlorination of *n*-propylbenzene, again using CCl_4 as the solvent [17]. Incidents of octachlorostyrene in the environment have been attributed to waste products from electrolytic chlorine production [18]. In the present example, it is interesting to note where the hexachlorobenzene and octachlorostyrene were found in the reaction tube. Hexachlorobenzene was found, as in the work of Stevenson and Rudman, at the exit of the reaction tube. In addition, hexachlorobenzene was also found at the entrance of the reaction tube, upstream from where the Cr_2O_3 was placed. The octachlorostyrene was only found upstream, and it deposited as separate needle-like crystals among the more abundant hexachlorobenzene crystals. This suggests that wherever it is formed in the reaction tube, it survives only if it diffuses to the cooler upstream portion of the reaction tube. We used a very low gas flow rate in our experiments. This may explain how octachlorostyrene was able to diffuse against the N_2/CCl_4 gas flow direction.

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